Application Guide to Safeguards Calorimetry

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APPLICATION GUIDE TO SAFEGUARDS CALORIMETRY

by

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ABSTRACT

Calorimetry is used as a nondestructive assay technique for determining the power output of heat-producing nuclear materials. The heat is produced by the decay of radioactive isotopes within the item. Calorimetric assay of plutonium-bearing and tritium items routinely obtains the highest precision and accuracy of all nondestructive assay (NDA) techniques, and the power calibration can be traceable to National Institute of Standards and Technology (NIST) through certified electrical standards. Because the heat-measurement result is completely independent of material and matrix type, it can be used on any material form or item matrix. Heat-flow calorimeters have been used to measure thermal powers from 0.5 mW (0.2 g low-burnup plutonium equivalent) to 1000 W for items ranging in size from less than 2.5 cm to 36 cm in diameter and up to 61 cm in length.

The focus of this guide is on heat-flow calorimetry, techniques and instrumentation, used for thermal power measurements. Specific topics include calorimetry applications, thermal power production, types of heat-flow calorimeters, calorimeter operation, calibration and biases, MultiCal data acquisition software, and measurement performance. The determination of effective specific power is also discussed, in lesser detail, since it is necessary for calorimetric assay.

The extensive use of heat-flow calorimeters for safeguards-related measurements at DOE facilities make it important to have a calorimetry application guide to be used for training new personnel and to provide a reference for experienced personnel involved in safeguards measurements.

I. Introduction

Calorimetric assay is the determination of the mass of radioactive material through the combined measurement of its thermal power by calorimetry, and if necessary, its isotopic composition by gamma spectroscopy or mass spectroscopy. Calorimetric assay has been routinely used at US and European facilities for plutonium process measurements and nuclear material accountability for the last 35 years [EI54, GU64, GU70, ANN15.22, AS1458, MA82, IAEA87]. Over two hundred heat-flow calorimeters developed under the Department of Energy (DOE), Office of Safeguards and Security (OSS) Technology Development Program have been built for use throughout the DOE complex and the world over the last 50 years. Currently a total of 60 Wheatstone bridge calorimeters are being used for accountability measurements of plutonium and tritium at Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), Rocky Flats, Hanford, Savannah River, and other sites. This guide will focus on heat-flow calorimetry, techniques and instrumentation, used for thermal power measurements. The determination of effective specific power will also be covered, in lesser detail, since it is necessary for calorimetric assay. The extensive use of heat-flow calorimeters for safeguards-related measurements at DOE facilities and the turnover of personnel make it important to have useful reference documentation for new individuals to continue to make routine calorimetric assays. It is also important to inform both new and experienced users of calorimetry of the new capabilities and uses of calorimetry.

Calorimetry is the quantitative measurement of heat. Applications of calorimetry include measurements of the specific heats of elements and compounds, phase-change enthalpies, and the rate of heat generation from radionuclides. The most successful radiometric calorimeter designs fit the general category of heat-flow calorimeters. A heat-flow calorimeter consists of a sample chamber insulated from a constant temperature environment by a thermal resistance and a means to measure the temperature difference across the thermal gradient produced by the thermal resistance and the heat generated by an item in the sample chamber.

DOE facilities use calorimeters to measure material in sealed storage containers (off-line) and to measure material in process (in-line). Calorimeters have been fabricated for use during material processing by mounting the calorimeter under glove boxes. Off-line calorimeters are essential for routine facility accountability measurements, evaluation of shipper/receiver differences, and measurement of difficult material categories with unknown and/or heterogeneous matrices. Transportable calorimeters have also been built that can be moved from area to area within a facility or between DOE facilities.

Measurement Application

Calorimetric assay is presently the most precise and accurate nondestructive assay (NDA) technique for the assay of many physical forms of plutonium and tritium. Calorimetry has been applied to a wide variety of plutonium-bearing solids including metals, alloys, oxides, fluorides, mixed plutonium-uranium oxides, mixed oxide fuel pins, waste, and scrap (e.g., ash, ash heels, salts, crucibles, and graphite scarfings) [RO81, RE91]. An

example of the importance of calorimetric assay of plutonium-bearing items at LANL is presented in Table 1.

Table 1. Measurement Methods for LANL Pu Inventory % for Each Material Form[1]				
Material form	Calorimetry + gamma spec	Analytical chemistry	Neutron counter + gamma spec	Segmented gamma scanner
Metal	71%	29%	0.3%	0%
Compounds pure	64%	35%	0.9%	0.3%
Compounds impure	72%	23%	2.6%	2.6%

[1]From LANL Material Accounting and Safeguards System (MASS) database April 1999.

Calorimetric assay has applications in a number of different areas:
a) shipper/receiver measurements,
b) accountability measurements,
c) calibration of NDA standards,
d) process control measurements,
e) outlier resolution, and
f) product acceptance measurements.

Of the items listed above, "c" and "e" can only be done nondestructively using calorimetry.

Calorimetric assay can be applied to a number of different radionuclides:
a) Plutonium isotopes,
b) HEU items (multi-kilogram sized),
c) ^{233}U,
d) ^{237}Np,
e) ^{242,244,245}Cm,
f) ^{250,252}Cf,
g) ^{241,242m,243}Am
h) tritium, and
i) fission products.

Calorimetric assay can be accurately used for any of the above-listed items that will fit in the instrument measurement well and are free from any exothermic or endothermic chemical reactions.

Calorimetric Assay Overview

Calorimetry is used as an NDA technique for determining the power output of heat-producing nuclear materials. The heat is generated by the decay of radioactive isotopes within the item. Calorimetric assay of plutonium-bearing items routinely obtains the highest precision and accuracy of all NDA techniques, and the power calibration can be traceable to National Institute of Standards and Technology (NIST) through certified electrical standards. Because the heat-measurement result is completely independent of material and matrix type, it can be used on any material form or item matrix. Heat-flow calorimeters have been used to measure thermal powers from 0.5 mW (0.2 g low-burnup

plutonium equivalent) to 1000 W for items ranging in size from less than 2.54 cm to 35.56 cm in diameter and up to 60.96 cm in length.

Heat-flow calorimeter designs developed under the OSS Technology Development Program are in extensive use throughout the DOE complex. These high-precision calorimeters are based on nickel-wire temperature sensors connected in a Wheatstone bridge configuration. A precision temperature-controlled water bath is commonly used to provide a constant reference temperature and infinite heatsink.

The item is placed in the calorimeter measurement chamber, and the total heat flux at equilibrium, i.e., the thermal power, from the item is determined by temperature sensors and associated electronic equipment. The thermal power emitted by a test item is directly related to the quantity of radioactive material in it, and the total power generated by ionizing radiation absorbed in the item is captured by the calorimeter. The mass (m) of plutonium, tritium, or ^{241}Am, is calculated from the measured thermal power of an item (W) using the relationship

$$m = \frac{W}{P_{eff}} \tag{1}$$

where P_{eff} is the effective specific power calculated from the isotopic composition of the item. The details of determining P_{eff} are discussed in Section III. For monoisotopic items, the specific power of the radioisotope is used in place of P_{eff}.

II. Uniqueness of Calorimetry NDA

Advantages

Calorimetric assay offers several distinct advantages over other NDA techniques and chemical analysis:

- The calorimeter heat measurement is completely independent of material and matrix type; self attenuation cannot occur.
- No physical standards representative of the materials being assayed are required.
- The thermal power measurement is traceable to the US or other National Measurement Systems through electrical standards used to directly calibrate the calorimeters or to calibrate secondary ^{238}Pu heat standards.
- Calorimetric assay can been used to prepare secondary standards for neutron and gamma-ray assay systems [IAEA87, AS1207, HY99, LE00].
- The heat from the entire item volume is measured. As a result, the response of a well designed calorimeter is independent of the location of the heat sources inside the measurement chamber.
- P_{eff} remains the same (with correction for nuclear decay) as long as the isotopic composition is not changed; therefore, the same P_{eff} is applicable to a batch of material regardless of form.
- Calorimetry is very precise and nearly bias free. Biases can be quantitatively determined during instrument calibration.
- Only nuclear criticality safety considerations and the volume of the measurement chamber limit the quantity of material that can be measured in a calorimeter.
- Calorimetric assay is the most accurate, NDA or otherwise, method for the measurement of tritium and ^{241}Am.
- Calorimetry is the only practical measurement technique available for many physical forms of tritium compounds.

Limitations

Calorimetric assay is largely independent of the elemental distribution of the nuclear materials in the matrix, but the accuracy of the method can be degraded for materials with inhomogeneous isotopic composition due to uncertainty in determining the effective specific power. Calorimetry measurement times are typically longer than other NDA techniques. The packaging conditions of the item cannot change the heat output of the material but are usually the determining factor for measurement time. Typical assay times are between one and eight hours. The calorimeter cannot distinguish between heat produced by radioactive decay and heat produced by other sources (e.g., phase changes and chemical reactions).

Heat from chemical reactions is generally not an issue since most items measured with calorimetric assay are hermetically sealed dry items. In addition, any large time dependence on the heat output would be an indication of heat from a chemical reaction.

III. Thermal Power Production in Radionuclides

Calorimetric assay is routinely used as a reliable NDA technique for the quantification of plutonium and tritium content within items. Plutonium items usually contain varying amounts of [241]Am, which can be accounted for during the assay. The principal decay modes, specific heats, half-lives, and the associated uncertainties are listed in Table 2 for all plutonium isotopes, [241]Am, and tritium. The majority of the heat measured by calorimetry is due to spontaneous alpha-particle emission, except for [241]Pu and tritium, which predominately decay via beta decay. Each radionuclide has a specific disintegration energy associated with its particular decay scheme; for example, [240]Pu decays to [236]U with the emission of an alpha particle and the release of 5.15 MeV energy. The rate of energy emission is equal to the product of the total decay energy and the activity. This product for a single radionuclide is called specific power, P, and is used to convert the power measurement into a mass of material. For multi-isotopic items, the analytical factor used to convert the heat measurement to mass of material is effective specific power, P_{eff}. The determination of specific power and effective specific power will be discussed in detail in the next two sub-sections.

Table 2. Nuclear Parameters of Commonly Assayed Nuclides.						
Isotope	Dominant Decay Mode[1]	Specific Power (mW/g)	% Std. Dev.	$T^{1/2}$ (y)	% Std. Dev.	References
[238]Pu	α	567.57	0.05	87.74	0.05	WA77,ST78
[239]Pu	α	1.9288	0.02	24119	0.11	ST78,SE78,GU78
[240]Pu	α	7.0824	0.03	6,564	0.17	RU84,LU84,BE84,ST84,JA78,ST84
[241]Pu	β	3.412	0.06	14.348	0.15	MA80,GA80,DE81,JO82,OE68
[242]Pu	α	0.1159	0.22	376,300	0.24	OS76
[241]Am	α	114.4	0.37	433.6	0.32	JO82,OE67
Tritium	β	324	0.14	12.3232	0.017	RU77

[1]For all of the nuclides listed the dominant decay mode has a branching ratio > 99.99%.

The total reaction energy for alpha decay is the sum of the alpha-particle kinetic energy, and the recoil energy of the daughter nucleus. The alpha particle and daughter nucleus have very short ranges in matter. Thus, virtually all of the energy released by alpha decay will remain within the item as heat. If the daughter product is not in the ground state as a result of the decay, an additional small amount of energy is released in the form of gamma-ray and internal conversion electron energy. The electron and low-energy gamma-ray energy is absorbed in the item and the item container. The upper limit on lost energy due to escaping gamma rays from plutonium and uranium isotopes and [241]Am are listed in Table 3. The relative heat contribution due to spontaneous fission energy using branching ratios and an average reaction Q value of 200 MeV are very small and are also listed in Table 3.

The maximum energy loss listed in the last column of Table 3 was calculated using the assumption that 20% of the spontaneous fission energy is completely lost from the calorimeter due to the escape of all neutrons and photons. This assumption is a large overestimate of the photon energy loss since all low-energy photons are attenuated in the item and calorimeter. The attenuation increases with increasing item size. [241]Am and [235]U show rather large calculated maximum energy fraction loss. For both nuclides, the large calculated maximum loss is dominated by the photon energy fraction. In the case of [241]Am, the 60-keV gamma ray accounts for more than 75% of the total gamma-ray energy, and virtually 100% of these gamma rays are completely attenuated in the item and item container. For the case of [235]U, over 65% of the total gamma-ray energy is due to the 186-keV gamma-ray emission. The heat measured from HEU items is predominately because of [234]U due to the low specific heats of the [235]U, [236]U, and [238]U nuclides listed in Table 3. Therefore, even if a large fraction of the [235]U heat is lost to gamma-ray emission, the overall loss of heat from the item is more than four orders of magnitude less significant than the heat from [234]U.

Another source of heat loss to consider is the loss of neutrons following (α, n) reactions; this loss can also be shown to be negligible even for high-efficiency radioisotope neutron generators. For example, the neutron yield for ^{9}Be(α, n) per 10^6 [241]Am alpha particles is 70. Assuming all the neutrons escape capture and using the fact that the average neutron energy is comparable to the Q-value of the original alpha decay, the fraction of lost heat would be 0.007%.

Table 3. Sources of Heat Other than Alpha Decay.					
Isotope	P (mW/g)	Photon Energy Fraction (%)[1]	SF[2] Branching Ratio (%)	SF[2] Energy Fraction (%)	Max. Energy Loss (%)[3]
[238]Pu	567.57	3.1E-02	1.8E-07	6.6E-06	3.1E-02
[239]Pu	1.9288	1.3E-03	3.0E-10	1.1E-08	1.3E-03
[240]Pu	7.0824	5.4E-04	5.8E-06	2.2E-04	5.8E-04
[241]Pu	3.412	2.5E-02	2.4E-14	8.7E-10	2.5E-02
[242]Pu	0.1159	2.8E-02	5.5E-04	2.2E-02	3.2E-02
[241]Am	114.4	0.509[4]	4.3E-10	1.5E-08	5.1E-01
[233]U	2.81E-01	2.6E-02	6.0E-11	2.4E-09	2.6E-02
[234]U	1.80E-01	2.3E-03	1.6E-09	6.8E-08	2.3E-03
[235]U	6.00E-05	3.33[5]	7.0E-09	3.0E-07	3.3E+00
[236]U	1.75E-03	3.3E-02	9.4E-08	4.1E-06	3.3E-02
[238]U	8.51E-06	3.0E-02	5.5E-05	2.6E-03	3.1E-02

[1]The energy loss due to gamma escape will be significantly less than total energy.
[2]Spontaneous fission.
[3]Maximum fractional energy loss due to escaping neutrons and gamma rays.
[4]0.39% of the total energy is from the 59.5364-keV gamma ray.
[5]2.2% of the total energy is from the 185.739-keV gamma ray.

Specific Power

The specific power, *P*, is the rate of energy emission by ionizing radiation per unit mass of a single radionuclide. Nuclear decay parameters can be used to calculate the *P*, in watts per gram, of a single radionuclide according to the equation

$$P = \frac{2119.3}{T_{1/2} * A} * Q \qquad (2)$$

where Q is the total disintegration energy (MeV) for alpha-particle emitters, or the average energy (MeV) of beta-particle emitters, $T_{1/2}$ is the half-life (years), and *A* is the gram atomic weight of the radionuclide. [241]Pu and tritium decay predominately via beta decay. The determination of energy losses in matter is more complicated for beta emitters than with alpha emitters. With beta decay, the total reaction energy is in the form of a beta particle, neutrino, and the excitation and recoil energy of the daughter. The energy loss due to bremsstrahlung radiation, emitted as a result of deceleration of the beta particle, is negligible for [241]Pu and tritium; therefore, nearly all of the kinetic energy of the beta particle is absorbed by the item as heat. The neutrino is not absorbed by the item or calorimeter, therefore its energy is not measured as heat. The thermal power measured by a calorimeter from beta-decaying radionuclides is the product of the activity and the average beta particle energy, which is on average one third of the maximum disintegration energy.

Specific power can also be determined empirically based on a total heat, *W*, measurement in watts of a single isotope, *i*, of known mass, m, of material in grams by rearrangement of Equation 1 to

$$P_i = \frac{W}{m} . \qquad (3)$$

The specific powers of a number of radionuclides are listed in Table 3. The values for the plutonium and americium isotopes were taken from ANSI N15.22. The uranium specific powers were calculated using Equation 2. Examination of Equation 3 shows that the specific power can be determined from direct measurement of an isotopically pure sample. The specific powers of [239]Pu, [240]Pu, [241]Pu, and [242]Pu were determined empirically on nearly pure isotopic samples. The [239]Pu and [240]Pu values were based on collaborative experiments [ST78, SE78, GU78, RU84, LU84, BE84, ST84, JA78, ST84A] while [241]Pu and [242]Pu specific powers were determined by individual experimenters [MA80, GA80, DE81, JO82, OE68, OS7620-25]. Equation 2 was used to calculate the specific power of [238]Pu and [241]Am [WA77, ST78, JO82, OE67].

The specific powers listed in Table 3 span a large range of values from a high of over half a watt per gram of [238]Pu to a low of less than 10 nW per gram of [238]U. The specific powers listed in Table 3 for the uranium isotopes were calculated using Equation 2. The magnitude of specific power is inversely proportional to the half-life of the radionuclides regardless of element. Specific power alone can be used to determine total radioactive material mass for items containing a single isotope. The total alpha activity of transuranic (TRU) materials can also be determined by using calorimetry independently [RU00].

Effective Specific Power

Most items other than tritium do not contain a single radioactive isotope but multiple isotopes and/or multiple radioactive elements. An effective specific power, P_{eff}, in units of power per unit mass must be obtained for these items. The most common example of items containing multiple radioactive elements is an item containing a mixture of plutonium and [241]Am. [241]Am is found in nearly all plutonium items due to the decay of [241]Pu into [241]Am.

The effective specific power of the material in the item is calculated by

$$P_{eff} = \sum_i R_i * P_i \qquad (4)$$

where:
- R_i is the abundance of the i-th radionuclide in the item, typically expressed as a mass fraction to a total elemental mass,
- i includes any heat producing radionuclide present, and
- P_i is the specific power of the i-th radionuclide in the item in watts/gram.

The heat producing mass of the item is

$$m = \frac{W}{P_{eff}} \qquad (5)$$

where W is the total power of the item in watts and P_{eff} is the effective specific power. The specific power of the isotope, P, is equivalent to P_{eff} for items containing a single radionuclide. For all multi-radionuclide items the effective specific power is not a constant and needs to be corrected for the decay and growth of the constituent radionuclides. See reference [RE91A] for details on decay correction of plutonium bearing items.

Two methods exist for determining effective specific power: a computational method and an empirical method. The computational method uses Equation 4 for determining effective specific power and is appropriate when isotopic composition measurements can be made. The relative abundances of the radionuclides can be determined destructively using mass spectroscopy [ANN104, ANN572, AS697] or nondestructively using gamma-ray spectroscopy [RE91B, AS1030]. When measuring items in sealed containers high-resolution gamma-ray spectroscopy using intrinsic germanium detectors is the only option for determining effective specific power. The uncertainties on P_{eff} using gamma-ray measurements for plutonium-bearing items are generally less than 0.5%. If mass spectroscopy is used to determine P_{eff} of plutonium-bearing items, the [238]Pu contents should be determined using alpha spectrometry [AS697A] and [241]Am contents should be determined radiochemically. The uncertainty of the results is normally 0.1%, for isotopically homogeneous items. The computational method using gamma-ray spectroscopy for isotopic analysis is the dominant technique used in conjunction with calorimetry.

The empirical method of determining the effective specific power involves a calorimeter measurement to determine the total power produced by the sample and a chemical

analysis to determine the total amount of nuclear material in the sample. Substituting these values into Equation 5 P_{eff} can be determined. The empirical method is potentially more accurate and precise than the computational method. The method can only realistically be implemented cost effectively on discrete batches of process materials or when it is difficult to determine the relative isotopic abundances of an item or batch of material. As with using mass spectroscopy in the computational method, the empirical method is a destructive technique that generates waste and requires long assay times to complete the analysis. These time and waste issues have increased the exclusive use of NDA techniques for the quantitative determination of special nuclear material (SNM) mass.

IV. Types of Heat-Flow Calorimeters

Figure 1. Schematic of calorimeter components.
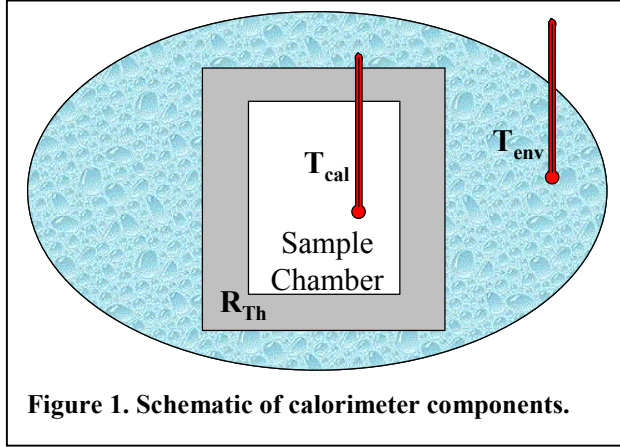
All calorimeters have four elements in common: 1) sample chamber, 2) well defined thermal resistance, 3) temperature sensor, and 4) environment. The interrelationship of these four components and the hardware that is used for each determine the type of calorimeter. A simple schematic of the components necessary for heat-flow calorimetry is shown in Figure 1. Radioactive material continuously produces heat at nearly a constant rate. There is some change due to decay and daughter products, but the time scale for measurable change is generally days to weeks. Therefore, the most appropriate calorimeter design for radioactive material is a heat-flow, isothermally jacketed, calorimeter. The design of the calorimeter is determined by the size and heat output of the items to be measured and the required accuracy in the heat measurement. Several basic heat-flow calorimeter designs and modes of operation are possible, such as gradient-bridge, twin-bridge, isothermal "Air Bath," and rod calorimeters operated in either servo or passive mode.

A heat-flow calorimeter is constructed so the heat generated in the calorimeter flows past a temperature-sensing element, through a well defined constant thermal resistance, to a constant-temperature heatsink. When an item is placed in the calorimeter the temperature gradient across the thermal resistance is disturbed and the gradient changes with time until it converges to a constant value and equilibrium is achieved. The heat produced in the sample chamber raises its temperature and causes heat to flow across the thermal resistance into the environment according to

$$\frac{dQ}{dt} = \frac{(T_{cal} - T_{env})}{R_{Th}} = \frac{\Delta T}{R_{Th}} \tag{6}$$

where Q is the heat energy, R_{Th} is the thermal resistance, T_{cal} is the internal calorimeter temperature, and T_{env} is the external environment temperature. At equilibrium dQ/dt is constant and ΔT, usually measured in volts, is proportional to the power of the item. The magnitude of the shift in the measured voltage (passive mode) or supplied power (servo mode) is used to determine the thermal power of the item in the calorimeter.

The curve describing the approach of the temperature difference to equilibrium is a function of several exponentials with different time constants. The time constants are related to the specific heats and thermal conductivities of the item matrix material, packaging, and, in some instances, the calorimeter. An example of a typical calorimeter approach to equilibrium is presented in Figure 2. Equilibrium may be detected by visual inspection of the measurement data vs. time or through statistical tests performed on a set of the latest data points in the time series. Statistical prediction algorithms may be used

Figure 2. Typical calorimeter sensor output after item insertion.
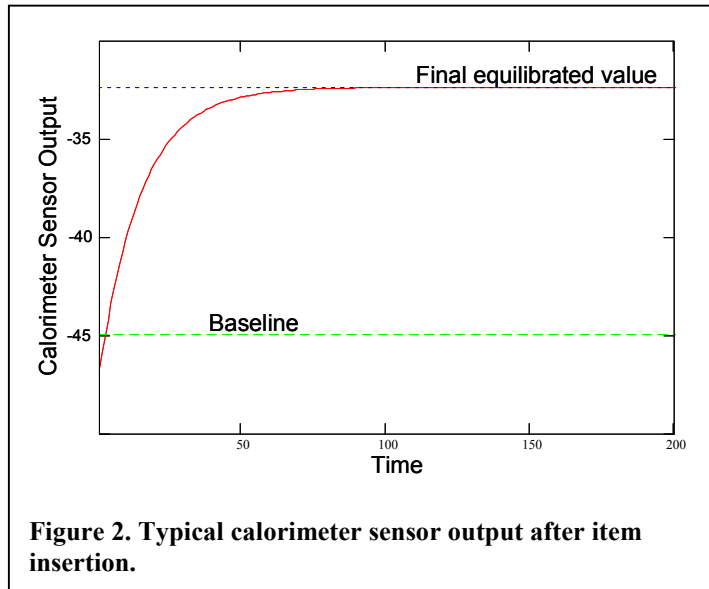
earlier during transient temperature conditions to predict equilibrium and reduce measurement time. These typically consist of exponential functions that are used to fit the measurement data. The fitted parameters are then used to predict the final equilibrium power. The temperature of the item to be measured may be adjusted using preconditioning baths to shorten the time required to reach equilibrium.

The type and placement of the temperature sensors, the heat-flow path, and the type of heatsink are what differentiates between types of heat-flow calorimeters used for measuring radionuclides. The heat flow is directed to areas where the sensors are located by the use of conductive and insulating material or controlling temperatures.

Different types of heat-flow calorimeter systems used for measuring SNM share many common attributes:

a) Measurement Chamber. Heat-flow calorimeters have a cylindrical measurement chamber from which all of the heat flow generated by radioactive decay is directed through temperature sensors.

b) Internal Heater. An electrical heater may be built into the walls or the base of the chamber to provide measured amounts of thermal power in the measurement chamber. In the case of servo-controlled calorimeters, the measurement chamber is maintained at a constant power level by use of the internal heaters. Internal heaters are used to simulate heat-producing radionuclides in passive-mode calorimeters.

c) Temperature Fluctuation Shielding. Insulation or servo-controlled heaters and/or coolers are used to shield the chamber from outside temperature variations that would influence the thermal power measurement. Typically, an insulated plug is inserted above the item container inside the calorimeter. For some calorimeter types, an insulating plug is permanently installed below the measurement chamber.

d) Calorimeter Can. The item to be measured is usually placed in a special can that is designed to be inserted and removed easily from the calorimeter. It has a minimal air gap to provide good thermal conductivity between the outer surface of the can and the inner surface of the measurement chamber. The can is also intended to prevent radioactive contamination of the inside of the calorimeter.

e) Temperature Sensors. Currently, the temperature sensors most commonly used are high-purity nickel wires in a Wheatstone bridge configuration. Other sensor types used are thermocouples, thermopiles, or, less commonly, thermistor chains. Each of

these sensors, when configured properly, is used to measure a temperature difference across a constant thermal resistance.

f) Heatsink. The temperature increases due to heat flows generated by items are measured against a reference temperature of a heatsink. Most calorimeters use a water bath as the infinite heatsink, but air or conductive material maintained at a constant temperature by a thermoelectric cooler/heater or resistance heater is also used in some designs.

g) Electrical Components. Sensitive, stable electronic components are required for accurate calorimeter measurements, including 1) high-precision voltmeters to measure the voltage changes generated by the temperature sensors; 2) stable power supplies to provide constant current to resistance sensors and calorimeter heaters. The resolution of the voltmeters should be better than 1 part per million of the voltage range.

h) Heat Standards. Precision resistors with certified resistances traceable to a national measurement system may be used with calibrated voltmeters to accurately determine electrical power delivered to heaters in the calorimeter chamber. If radioactive heat standards are used as part of the measurement control program, the calorimeter voltmeters need not be calibrated, nor are precision resistors required.

i) Servo Power Delivery. For a calorimeter operated in the servo mode, digital-to-analog controller units are used to supply power to an internal resistance heater to maintain constant temperature differentials across thermal resistances.

j) Data Acquisition System. Calorimeter data collection is performed using computer-based data acquisition systems. The system should be able to read signal voltages or resistances at a fixed time frequency and be able to calculate and report a power value from the item using software that detects equilibrium. Graphics and numerical data indicating system power and temperatures may be displayed to aid the operator.

k) Adapters. Cylindrical metal adapters may be fabricated to accept smaller calorimeter containers in the calorimeter well and thus provide good thermal contact between the outer container surface and calorimeter inner wall. Heat-conducting metal foil, gauze, or shot, typically Al or Cu, can be used in place of machined metal adapters. When these materials are used to fill the void space, smaller items may be placed in the calorimeter container and still maintain good thermal contact. Under the same measurement conditions fill materials with less thermal mass will result in shorter measurement times than materials with larger thermal mass.

A variety of heat-flow calorimeter designs has been used to measure nuclear material. Four major types of designs that have been used for accountability measurements are 1) water-bath calorimeters, 2) solid-state calorimeters, 3) isothermal "air bath" calorimeters, and 4) rod calorimeters. The air-bath and rod calorimeters described below have been operated exclusively in the servo mode, and the water-bath calorimeters have been operated in the passive or servo mode. Solid-state calorimeters can be operated in passive or servo mode if internal heaters are built into the design.

Water-Bath Calorimeter

The elements common to all current water-bath calorimeters are labeled in Fig. 3, using a cutaway drawing of a twin-bridge, water-bath calorimeter. The components are described starting from the innermost elements in Fig. 3. The measurement chamber (sample and reference) is occupied by a removable calorimeter can that holds the item being assayed and provides good thermal contact with the chamber wall while preventing any potential contamination of the inside of the calorimeter. If an internal heater is specified in the calorimeter design, the circumferences of both measurement chambers are wound with manganin wire, which is used as the internal calorimeter heater. Two lengths of nickel wire are wound concentrically about the internal heater windings and serve as two sensor arms of the Wheatstone bridge. The thermal resistance between the sample sensor windings and the water bath are identical to the thermal resistance between the reference sensor windings and the water bath. This thermal resistance matching is done to maximize cancellation of water-bath temperature fluctuations in the Wheatstone bridge. The sensitivity of the calorimeter is directly proportional to the thermal resistance of the thermal gap. The thermal gap material usually consists of up to 0.3 cm of air or up to 1.0 cm of epoxy, for either type of calorimeter. The wider the thermal gap, the larger the internal temperature rise of the sample chamber for a given thermal power. The insulating material at the top and bottom of the measurement cells is used to force all of the heat radially through the sensing element.

Figure 3. Schematic of a twin-bridge heat-flow calorimeter with basic components labeled.
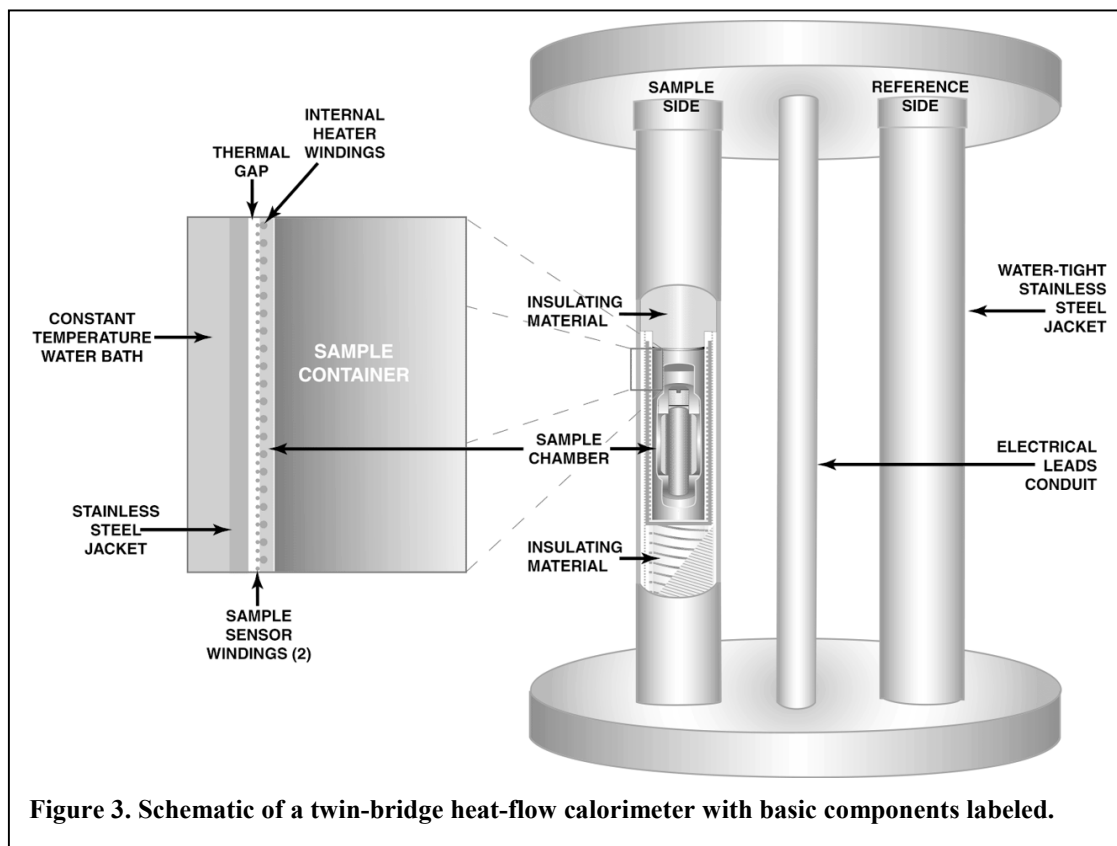
The outermost surface of the calorimeter is a stainless steel jacket. The stainless steel jacket is used to keep the inside of the calorimeter dry when submerged in the water bath.

A water bath with stirrer or circulating pump is used to maintain a constant reference temperature and serves as a heatsink. The water-bath reference temperature is maintained using feedback servo control. These units may use refrigeration compressors, resistance heaters, thermoelectric cooling units, evaporative cooling, or any combination of the above-listed for temperature control. The thermally stable reference bath is controlled to better than ±0.001°C, which is critical to high-precision, low-power measurements.

R_S=Resistance of sample arm
R_R=Resistance of reference arm

Figure 4. Balanced Wheatstone bridge circuit.
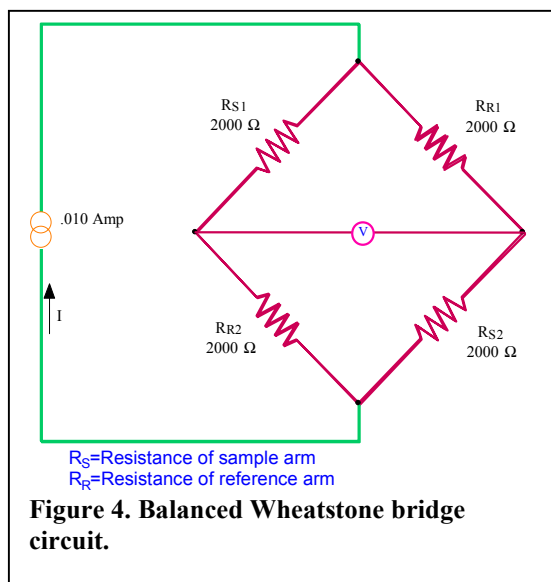
Twin- and gradient-bridge are the two broad classes of water-bath calorimeters commonly used in United States DOE laboratories and facilities. For both types of calorimeters, the Wheatstone bridge circuit shown in Figure 4 is used to measure heat flow. The reference and sample arms of the bridge are wound with high-purity nickel wire. The change in resistance with temperature is linear with a sensitivity of about +0.6% per °C. The temperature rise in the sample side due to the presence of radioactive material causes the resistance of the sample arms of the Wheatstone bridge to increase while the resistances of the reference arms remain constant. This resistance change causes an imbalance in the bridge and the voltage across the bridge (the bridge potential) changes in proportion to the size of the temperature change. The reference sensor wire arms and sample sensor wire arms of the Wheatstone Bridge are each helically wound interleaved (bifilar winding) and concentrically around a cylindrical chamber. The differentiation between twin- and gradient-bridge is made based on where the arms of the Wheatstone bridge are placed relative to each other. In the twin-bridge configuration, two windings are on one measurement chamber and two windings are on an identical measurement chamber as in Figure 3. A schematic of a gradient-bridge calorimeter is presented in Figure 5. In this case the two windings are wound concentrically about the inner pair of windings with a thermal gap between the two pairs. Twin-bridge calorimeters have also been built with the reference thermel located under and coaxial to the sample thermel ("over-under" design) to save space. This configuration is also presented in Figure 5.

Twin-bridge calorimeters are usually placed in a large (550–1000 liters) water bath to provide a stable reference temperature. These water baths are mixed using a propeller on a shaft rotated by a motor. Multiple calorimeters have been fitted into one water bath. For heat-flow calorimeters using a water-bath reference temperature, the identical windings on the reference chamber are used as a fixed reference resistance for two arms of a Wheatstone bridge while the sample sensor windings around the sample chamber change resistance due to heat flow from the sample. Small reference-bath temperature fluctuations are further corrected for by the twin-bridge design. Because both the reference and sample windings have identical thermal heat paths to the reference bath,

any resistance changes in the windings due to temperature fluctuations are canceled in the twin-bridge configuration.

Figure 5. Schematic diagram of gradient and over-under Wheatstone bridge calorimeter.
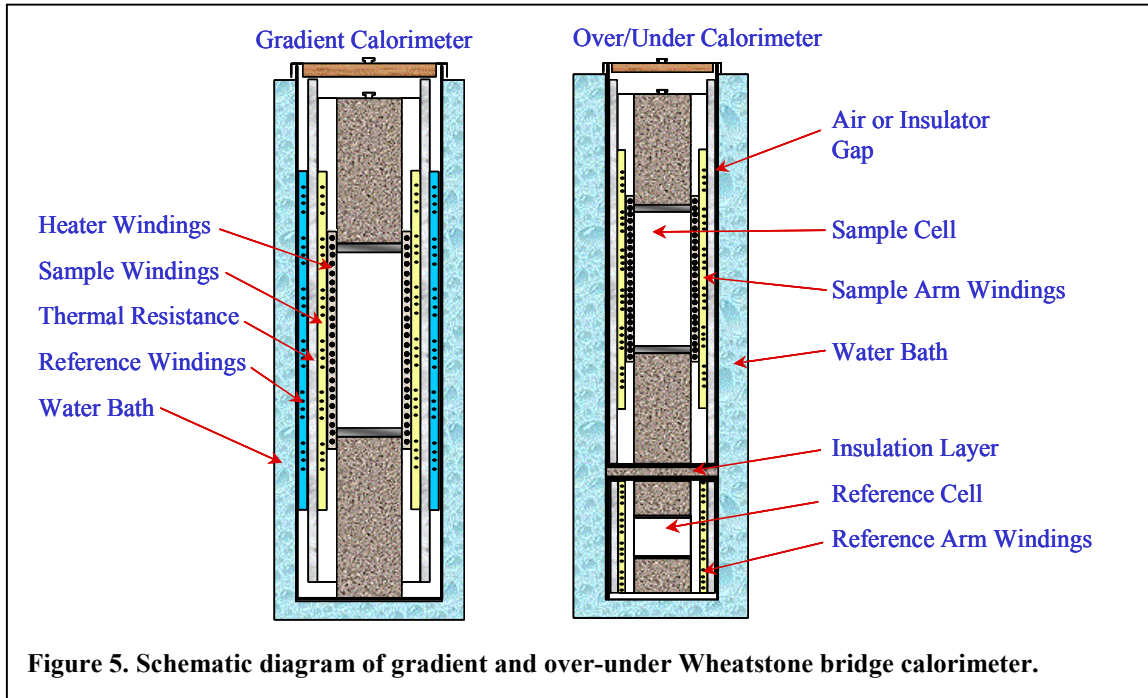
Gradient-bridge calorimeters usually have circulating water through an outer jacket of the calorimeter connected to a separate temperature conditioning system via connecting hoses. Smaller volumes of water, less than 76 liters, are required for this type of water-bath system. The smaller water volumes and connecting hoses increase the reference temperature noise due to ambient room-temperature fluctuations. Also, with the gradient design, cancellation of reference temperature fluctuations are not maximized due to the time lag between when the reference arms of the bridge change resistance due to temperature change and the time the sample windings change resistance due to the same temperature change of the water bath. Although the gradient calorimeter is more sensitive to bath temperature fluctuations, for higher-power measurements these fluctuations do not add significantly to the measurement uncertainty.

A block diagram of the instrumentation and communication typically used to operate a Wheatstone bridge calorimeter is presented in Figure 6. All of the electronics used are standard, commercially produced items. A 7.5-digit digital multimeter is used to readout bridge potential and 6.5-digit multimeters are used to readout bath temperature, bridge current, and room temperature. A General Purpose Interface Bus (GPIB) bus is used as the communication link between the electronics and the computer.

Figure 6. Typical Wheatstone bridge calorimeter electrical and communication configuration.
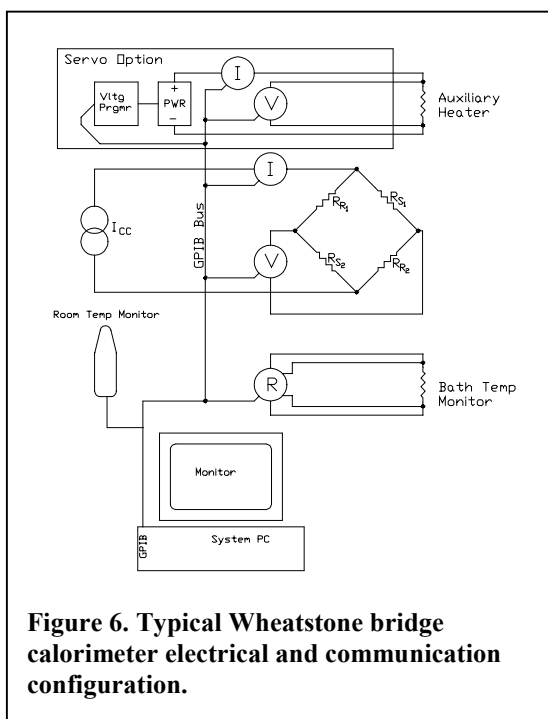
The advantages of twin-bridge calorimeters compared to gradient-bridge are listed below:
a) best cancellation of thermal effects,
b) lowest standard deviation of bridge potential,
c) lowest detection limits,
d) best precision and accuracy, and
e) long-term stability.

Advantages of gradient-bridge calorimeters compared to twin-bridge:
a) smallest footprint,
b) uses fewest materials in construction,
c) more suited to closed bath system, and
d) makes the smallest transportable calorimeter.

Solid-State Calorimeter

Solid-state calorimeters use thermopile components as heat flow sensors. A thermopile consists of numerous thermocouple pairs electrically connected in series. Thermocouples are formed by electrically joining one set of ends of two dissimilar conductors or semiconductors. A temperature difference between two thermocouple junctions causes the development of an electromotive force, known as the relative Seebeck effect that is proportional to the temperature difference. The greater the temperature difference, the larger the voltage measured from the sensor.

Figure 7. High-precision solid-state calorimeter in a water bath. The IBM laptop in the foreground is used for data acquisition.
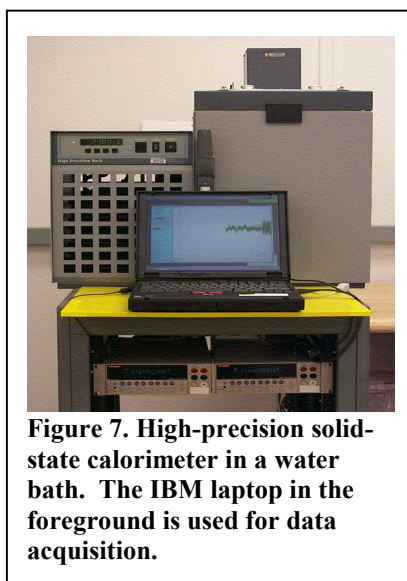
A picture of a small-sample, solid-state calorimeter is presented in Figure 7. This calorimeter uses thermopile heat-flow sensors. It was designed and fabricated at Los Alamos National Laboratory (LANL) with support from OSS. This portable calorimeter is designated the Solid-State Calorimeter System. It was fabricated from commercially available components and is capable of making high-precision measurements comparable to those made using much larger heat standards calorimeters. The data-collection electronics for the solid-state calorimeter system are commercially purchased digital voltmeters. Another benefit of using high-sensitivity thermopile sensors in calorimetric NDA systems is that the calorimeters are more robust, with excellent portability and baseline stability.

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A matched pair of thermopile heat-flow sensors is used as a replacement for the more commonly used Wheatstone bridge sensors. The availability of commercially produced high-sensitivity thermopile sensors has made them a viable alternative to the high-purity nickel wire used in a Wheatstone bridge sensor. With the passive thermopile sensor there is no self-heating of the calorimeter as there is with the constant current applied to a Wheatstone bridge. Without self-heating, more accurate measurement of low-power items can be made. The sensors are used in a twin configuration where one cylinder is used as a reference chamber for the cylinder that contains the heat-producing item. The electrical difference between the sample thermopile output and the reference thermopile output is measured using a nanovoltmeter. A water bath is used as a constant temperature heatsink, and when drained the system is portable. After moving, the calorimeter is ready to make measurements within 24 hours.

With a source power of ~10 mW, equivalent to 4 grams of low-burnup plutonium, the relative standard deviation of six measurements using the solid-state calorimeter system was 0.11%. The extremely low noise of the heat-flow sensor has a standard deviation range of 0.1 to 0.2 μV, allowing for high-precision measurements of items with powers in the submilliwatt range. The sensor response to heat is linear.

The advantages of thermopile heat-flow sensors compared to Wheatstone bridge sensors include the following:
   a) lower cost,
   b) wide commercial availability,
   c) scalability to any size or shape,
   d) passive signal,
   e) insensitivity to mechanical strains,
   f) intrinsically low noise,
   g) stable baseline (zero power output),
   h) increased portability,
   i) increased robust, and
   j) no sensor self-heating.
The extremely stable baseline value makes it possible to reduce the frequency of or eliminate baseline measurements.

Isothermal "Air-Bath" Calorimeter

Isothermal (constant temperature) air-bath calorimeters consist of three concentric cylinders separated by a heat-transfer medium. Each of the cylinders is equipped with temperature sensors. Nickel sensor wire and/or chains of thermistors may be used. The outermost cylinder is surrounded by a controlled temperature air bath rather than a water bath. The temperature sensors are measured using conventional Wheatstone bridge circuitry or by direct resistance measurement using a high-resolution multimeter. Power to control the temperature of each of the cylinders is supplied by power amplifiers. Heater coils are wound around each cylinder for this purpose.

The isothermal calorimeter operates such that each of the three concentric cylinders is at a successively lower temperature as one moves from the inner cylinder (measurement

chamber) to the outer cylinder. This difference in temperature results in a temperature gradient and heat flow from the inner cylinder to the outer cylinder. The calorimeter operates in servo mode. The system controller works to maintain a constant total thermal power in the measurement chamber. The total thermal power present in the measurement chamber is the power due to the internal heaters and the power due to the item being measured. The inner cylinder or measurement chamber of the calorimeter is operated at a fixed value known as the basepower. This basepower is the power supplied to the measurement chamber with no item present. The basepower must be confirmed periodically because the measurement is based on the difference between the basepower and the final equilibrium or predicted power of the measurement chamber. Isolation from the thermal environment is achieved by circulating air through an exterior chamber either by forced air cooling using room temperature air or by a closed-loop air circuit employing a thermoelectric cooling unit to provide a sufficiently low heatsink temperature [AS1458].

Rod Calorimeter

The thermal unit of the rod calorimeter is composed of a sample chamber, item insertion/removal plug, thermal shielding, and a highly controlled heat removal path. The calorimeter is operated in the servo mode. The heat removal path is through a highly conductive (typically copper) solid rod across which a constant temperature differential is maintained. The upper end of the rod, located at the base of the measurement chamber, is held at a constant temperature by supplying heat to the base (or side) of the measurement chamber. The lower end is held to a lower temperature, which creates a constant temperature differential. The thermal power supplied to the base of the measurement chamber is measured.

The thermal shield is composed of several components. The purpose of the thermal shield is to create a zero heat-transfer envelope around the measurement chamber with the exception of a highly controlled heat removal path through the copper rod. Multiple constant-temperature thermal shields may be used. Depending on the ambient temperature variations, one or two shields may be incorporated. For lower power measurements, the outermost constant temperature shield is typically a controlled temperature enclosure. Temperature measurements are made using high-precision resistance measurements of a thermistor. The plug used to insulate the item being measured is a component of the zero heat-transfer envelope and mitigates thermal effects resulting from gaseous pressure differentials in the measurement chamber.

The thermal unit uses from 4–12 closed-loop control systems for control of the thermal shielding and heat removal. Control requires temperature measurement, computer control algorithms with digital-to-analog (D/A) conversion, and power supplies for driving the heaters and coolers of the thermal unit. The computer D/A outputs are connected to power supplies for driving the heaters/coolers. The power supplies are high grade, low noise, and configured in an operational amplifier mode. System stability analysis is automated and based on power variations and temperature indicators [AS1458].

V. Possible Sources of Bias Due to Calorimeter Design

The following sections will describe possible sources of bias during calorimetry measurements. For most calorimeter designs, these effects are negligible but their magnitude should be quantified for all calorimeters. If a measurable effect is observed, the bias should be corrected by creating a bias correction curve across the range of the parameter being characterized.

Weight Effects

A shift in the calorimeter signal proportional to the mass of the item in the sample chamber is known as the "weight effect." The shift is caused by stressing the temperature-sensing element of the calorimeter and is typically linear with mass. To evaluate this effect, a series of paired baseline measurements is made. First, the baseline is measured with the sample chamber empty. Second, the baseline is measured with the sample chamber loaded with non-heat-producing material of approximately the same mass as the heaviest items to be assayed. If an effect is observed, further tests should be performed at other masses to verify the linearity of the effect. Bias corrections can be made for weight effects by weighing the item to be measured and making the correction to the calorimeter output. If a weight effect is observed, the bias correction factor should be confirmed periodically as a part of the measurement control program for the calorimeter.

Well-designed modern calorimeters should not show a weight effect. Weight effect can be identified with a single measurement of significant mass after the calorimeter has been fabricated. If a weight effect is not observed for a calorimeter, it does not need to be reevaluated.

Heat Distribution Error (HDE)

Heat distribution error (HDE) is a variation in the calorimeter response due to the location of the heat source within the measurement chamber. For example, the same heat source may produce a larger calorimeter output in the bottom of the sample chamber than in the top. The HDE could lead to a bias if the source location is unknown. HDE is quantified by measuring the same heat source placed at different vertical positions within the calorimeter can. Multiple measurements may be necessary to determine if the calorimeter output for the various positions is statistically different or the same. The power of the heat source should be the same or greater than the highest expected power of the items to be measured. The magnitude of an HDE will increase with increasing power. If an HDE is measured, the bias must be included in the final uncertainty of the power determination. An HDE can be minimized or removed by fabricating thick-walled calorimeter cans if a reduction in sample chamber size can be accommodated. Another possible solution to HDE is placing additional insulation at the top and/or bottom of the measurement chamber. The magnitude, polarity (loss or gain), and position of the HDE dictates which solution is best suited for a particular HDE. Well-designed calorimeters should not show an HDE.

Heater-Lead Error

Heater-lead error is potentially present for any calorimeter designed with built-in heaters or using insertable heaters. Even though the heater may be removable, the electrical leads should always be part of the calorimeter even during sample runs, because the heat loss or gain through the electrical leads is present when the heater is in use. If they are not present during item measurements, the thermal resistance of the calorimeter is changed and the electrical calibration is no longer valid. The magnitude and outcome of the effect is dependent on the design of the calorimeter (i.e., twin or gradient) and heater (insertable or fixed), the powers being measured, and what the heaters are used for (i.e., calibration, servo mode, or calorimeter response check). For electrical calibration purposes, a four-terminal heater should be employed with two current-carrying leads and two leads for making potential measurements. The same size, type, and length of wire should be used for these leads so that the lead errors can be measured and compensated for. The use of identical wire is also necessary for heater-lead heat generation and leakage compensation in twin calorimeters. The heater circuit used in twin calorimeters is shown in Figure 8. In the configuration shown in Figure 8, passing the same current through two leads on each side of the twin calorimeter compensates for the heat generated in the leads of the calibration heater. The heater leads are usually not brought directly out of the calorimeter. The leads usually exit the calorimeter along a path that maximizes the heater-lead contact with the controlled environment. This configuration is usually accomplished by winding around the circumference of the calorimeter, as physically close to the reference temperature as possible. The heater leads should be of low-electrical resistance compared to the heater to reduce heater-lead resistive heating. The use of low-resistance copper leads minimizes electrical resistance but also constitutes a heat-leakage path out of the calorimeter, potentially leading to an electrical calibration that is biased low.

Figure 8. Twin calorimeter heater-circuit diagram.
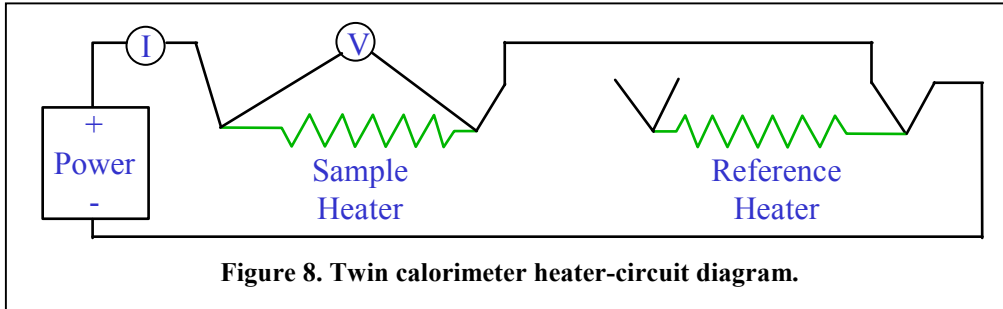
Estimation of calorimeter heater-lead heat in gradient calorimeters is accomplished by passing a series of different currents through one current lead and out the corresponding potential lead in series. The calorimeter output at each current is compared to the calorimeter zero. The correction for the heater-lead errors should be calculated from

$$\frac{V_i - V_0}{S_i} = a\left(I_i^2 R_h\right) \tag{7}$$

where V_i is the calorimeter sensor signal with measured current, I_i, in the leads, V_0 is the sensor signal with no current in leads, S_i is the sensitivity, a is a proportionality constant relating the heat in leads to that from the heater resistance, and R_h is the heater resistance.

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When the internal or insertable heater is used for calibration, the high-impedance digital voltmeters used for voltage and current measurements must be calibrated against certified electrical reference standards. If current is measured indirectly via a voltage drop across a calibrated resistor, the resistor must be a certified standard resistor. A stable high-precision power supply must be used to supply power to the heater. The calibrated voltmeter(s) and, if used, resistor must be recertified with a frequency consistent with facility-defined metrology practices.

If electrical heaters are used for calibration, a check of heater bias should be made against a certified heat standard. This check is most important for high powers, greater than a few watts, and very small powers, less than 200 mW. The cross measurement should be done if any portion of the heater circuit is changed or a new calibration is made.

VI. Methods of Operation

Heat-flow calorimeters are typically operated in one of two modes, passive or servo controlled, also known as power-replacement and active modes.

Passive Mode

In the passive mode, the most basic mode of operation, an item is placed in a calorimeter can, usually made of aluminum, which is inserted into the sample chamber of the calorimeter. The only generated heat comes from the item being measured, and if a Wheatstone bridge sensor is used, the small resistance heating of the sensors due to the current required to excite the bridge inside the thermel. The plot in Figure 9 shows that after a period of time the transient response caused by the insertion of the item into the calorimeter disappears as the calorimeter and item reach thermal equilibrium.

The item wattage, W_i, is calculated by

$$W_i = \frac{BP_s - BP_0}{S_0 + k\,W_i} \tag{8}$$

where BP_s is the equilibrium bridge potential with the item in the calorimeter, BP_0 is the baseline bridge potential with no item in the calorimeter, S_0 is the estimated sensitivity for zero power, and k is the slope of the varying sensitivity. The determination of S_0 and k is described in Section VII.

Figure 9. Typical Wheatstone bridge calorimeter approach to equilibrium.

Servo Mode

Figure 10. Schematic diagram of calorimeter digital servo control.
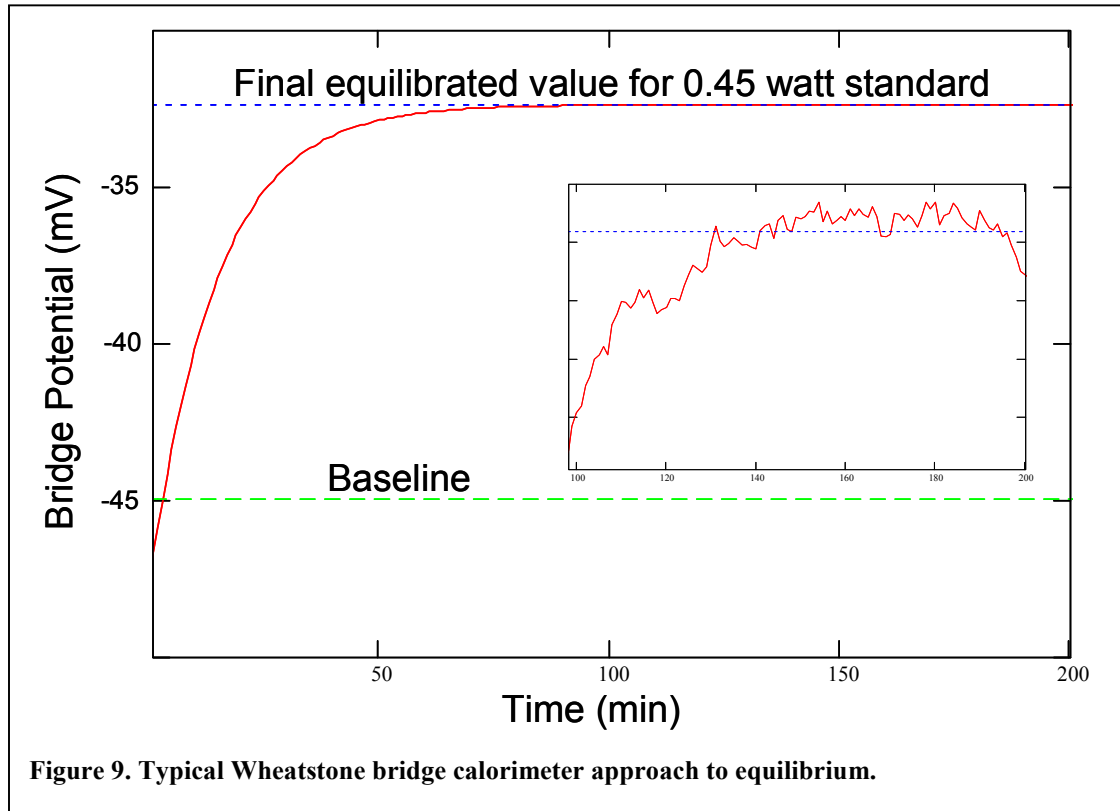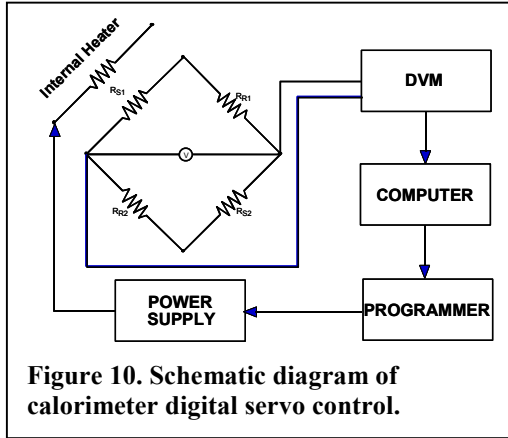
In servo mode, the inside of the calorimeter is maintained at a constant temperature via the internal heater and a servo-controlled feedback signal. A schematic flow diagram for calorimeter digital servo-control is presented in Figure 10. The digital voltage meter measures the signal from the Wheatstone bridge. The voltage reading is sent to the computer and compared to a control point voltage. The magnitude and sign of the difference between the reading and control point determines the adjustment made to the heater via the programmer and power supply. The temperature of the calorimeter measurement chamber is held several degrees above the temperature of the constant-temperature heatsink. The constant-temperature differential is proportional to the sensor signal (voltage or resistance). When a heat-generating item is inserted into the measurement chamber, the external power applied by the closed-loop controller is decreased to precisely maintain the same signal differential. The controller power drops over time until the calorimeter and item come back to the original internal temperature of the calorimeter. The power of the item being measured is the difference between the two control power readings at equilibrium.

The item wattage, W_i, is calculated by

$$W_i = W_0 - W_H \qquad (9)$$

where W_0 is the basepower with no item in the calorimeter and W_H is the power supplied to the calorimeter with the item in the calorimeter. The power supplied to the internal heater during the measurement of an item is presented in Figure 11 with the parameters used to calculate item power in Equation 9 labeled. The measurement time for the servo mode of operation can be shorter than for the passive mode because the calorimeter components are at the equilibrium temperature and the servo-controlled internal heater can supply heat to actively bring the item to equilibrium.

Figure 11. Internal heater power during the measurement of an item using a servo-controlled calorimeter.
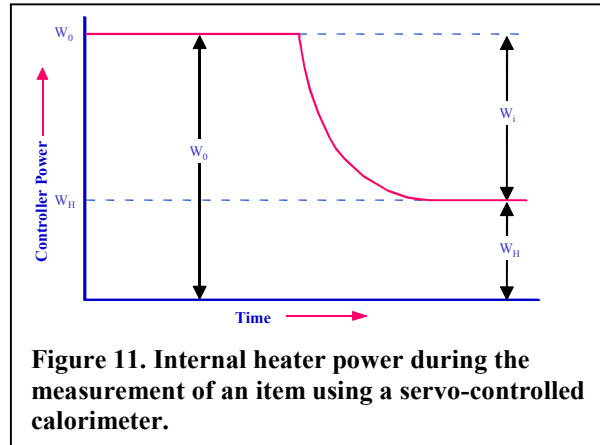
VII. Calorimeter Calibration Procedure

Calibration of a calorimeter is necessary to determine the power of an unknown item from the observed calorimeter output. Two types of heat standards are commonly used to calibrate calorimeters. The most reliable type of heat standard is a radioactive source of known power whose calibration is traceable to the NIST. These standards are normally made from ^{238}Pu and are made from well characterized—chemically and physically—materials. ^{238}Pu heat standards are used for calibrations more frequently than electrical-resistance heaters. Electrical heat standards contain an electrical circuit consisting of standard resistors and standard voltage cells. Such standards are also traceable to the NIST or other national measurement system. The resistor is used in place of a radioactive source, and the power dissipated in an electrical heater is measured using calibrated meters and calibrated resistors.

The type of calibration procedure depends on whether the calorimeter is operated in the servo or passive mode. In the passive mode, calibration consists of determining the calorimeter sensitivity, S, the conversion factor between the differential voltage or resistance output of the sensor system and the thermal power of the item being measured. In the servo mode, calibration is setting the sensor output setpoint voltage that corresponds to a specific base power and determining the stability of the heater power. During all calibration measurements, the calorimeter should be operated in the same manner used to make calorimetry measurements on items, as described in detail in the following sub-section.

Passive Mode

Whether radioactive heat standards or electrical calibration heaters are used, a series of calibration points equally spaced over the expected calorimeter operating range should be measured. The number of points will depend on the magnitude of the calorimeter differential sensitivity and the calibration accuracy required. A minimum of three different standard powers should be used. The form of the calibration curve varies according to the calorimeter design but is usually well represented by a quadratic function.

A baseline measurement of the zero power calorimeter output is made. This measurement is done with the calorimeter can filled with conductive material and no heat source. The equilibrium value of the calorimeter output is recorded as the baseline, $BP_{0(1)}$. A ^{238}Pu heat standard or an electrical resistance heater is then placed in the center of the calorimeter can. A measurement is started, and the equilibrium sensor output is recorded as BP_{std}. A baseline measurement is made after removing the heat source from the calorimeter can and recorded as $BP_{0(2)}$. Whether using radioactive or electrical heat standards, the calorimeter can must be removed from the calorimeter and opened between each measurement, baseline or standard. This removal is necessary even when using electrical standards to simulate as closely as possible real calorimeter operating conditions.

The average baseline, $BP_{0(av)}$ is calculated using

$$BP_{0(av)} = \frac{BP_{0(1)} + BP_{0(2)}}{2}.$$ (10)

Using the known power output of the ^{238}Pu heat or electrical standard, W_{std}, the calorimeter sensor value, BP_{std}, and the calculated average baseline, $BP_{0(av)}$, the sensitivity of the calorimeter can be calculated using

$$S = \frac{BP_{std} - BP_{0(av)}}{W_{std}}.$$ (11)

The sensitivity, S, is not usually a constant but varies slightly with the wattage of the standard, W_{std}, over the measurement range of the calorimeter. The change in sensitivity with power is described by

$$S = S_0 + k * W_{std}$$ (12)

where S_0 is the estimated sensitivity for zero power and k is the slope of the varying sensitivity. For most calorimeters, the magnitude of k is less than 1% of the zero power sensitivity over the operating power range. The sensitivity usually decreases with increasing power, which is qualitatively consistent with increased thermal conductivity of material forming the primary thermal resistance. For example the conductivity of dry air, a common thermal-gap material, increases at the rate of 0.3% per °C. The intrinsic high-order nonlinearity of thermopile sensors can lead to differential sensitivities that are negative or positive but still relatively small compared to the base sensitivity.

Three replicate measurements (minimum) are made at each power level, with each standard measurement bracketed by a baseline measurement as previously detailed. This detailed sensitivity determination at different power levels is typically done once after a calorimeter is fabricated. By combining Equations 11 and 12 and rearranging for net sensor output, $BP_{std}-BP_{0(av)}$, the equation to relate sensor output to watts is

$$\left(BP_{std} - BP_{0(av)}\right) = S_0 * W_{std} + k * W_{std}^2.$$ (13)

The fit parameters S_0 and k are determined by a least-squares fit to a plot of net sensor output as a function of standard watts. Since calorimeter noise is a function of the power of the item being measured, increasing variability with increasing power, the residuals of the least-squares fit will not be normally distributed. However the parameter estimates are not affected by this problem.

Actual calibration data used to determine the fit parameters in Equation 13 are presented in Figure 12. The data presented in Figure 12 were obtained using a twin-bridge water-bath calorimeter. Three to five heat standards measurements were made at each power. The linearity of the calorimeter response to power is typical of water-bath calorimeters.

A plot of the first derivative of calorimeter calibration data is normally designated a differential sensitivity plot. The data from Figure 12 is presented in Figure 13 as such a plot. It is easier to visually quantify the differential sensitivity of the calorimeter and the relative precision of the measurements at the different powers on a differential sensitivity plot than it would be from the plot in Figure 12. It is apparent in the plot in Figure 13 that

multiple measurements were made using the three lowest-power heat standards; this observation is not possible in Figure 12. The precision of this calorimeter is good enough that the multiple measurements, three each, at the largest two powers are not resolved on this scale.

$$\Delta V = 3.00\text{E-}05 * W^2 + 2.84\text{E-}02 * W$$

Figure 12. Calibration data for a twin-bridge water-bath calorimeter. The solid line is a quadratic least-squares fit to the diamonds.

Figure 13. Differential sensitivity plot of data presented in Figure 12. The solid line is a linear least-squares fit to the data.
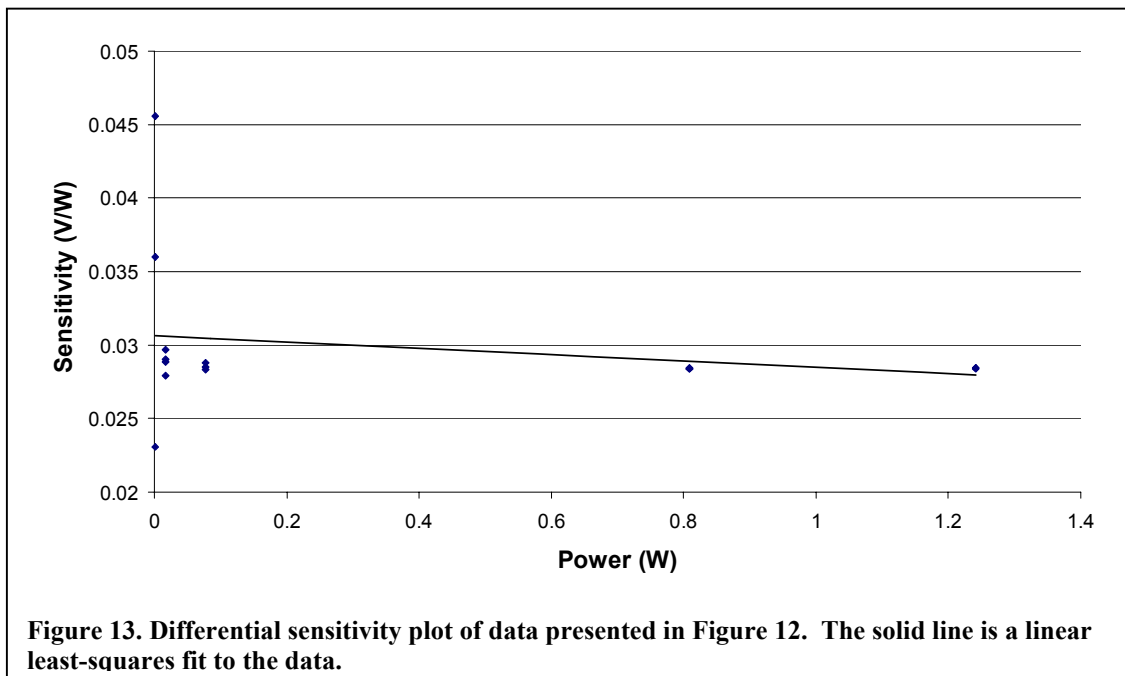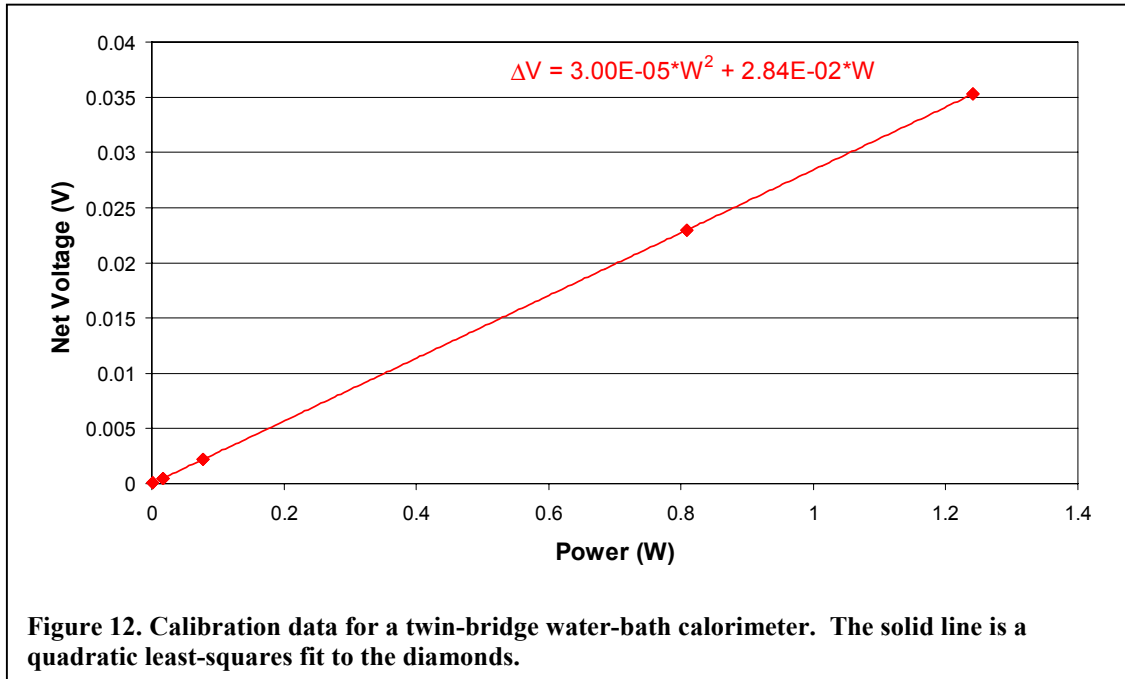
Servo Mode

The base power, W, of the calorimeter should be set 10–20% higher than the highest-power item expected to be measured. If the basepower is set less than the power of the

item to be measured, the calorimeter will not be operating in servo control at equilibrium, and a power determination cannot be made. A servo-controlled calorimeter can be used in passive mode if it has been calibrated as described above.

A single sensitivity point, S, must be determined by making a single measurement of a ^{238}Pu or electrical heat standard. Any power within the operating range of the calorimeter is satisfactory. $BP_{0(av)}$ is determined as it was for passive mode. The bridge potential setpoint (BP_{sp}) is calculated using

$$BP_{sp} = BP_{0(av)} + S*W \; .$$
(14)

The heater power is servo controlled to maintain a constant sensor output equal to BP_{sp}. The actual supplied heater power (W_0) used to maintain BP_{sp} may be slightly different from the target value, W, because of the uncertainty in S used to calculate the setpoint. Measuring a standard power that is as close as possible to the value of W will minimize the difference between W and W_0.

The item power is the difference between the measured basepower, W_0, with no item in the calorimeter and the measured heater power, W_H, at equilibrium with item present, according to Equation 9. Therefore, carefully matching W and W_0 will not increase the performance of the calorimeter in any way; it will only minimize the difference between the requested basepower and the actual basepower.

The basepower, W_0, is determined the same way as a baseline is determined in passive mode. The calorimeter can is filled with a conductive material and no heat generating items. The heater power measurement at equilibrium is the basepower, W_0, corresponding to BP_{sp}. Replicate measurements should be made of the basepower to determine the standard deviation of the value. The calorimeter can must be removed between repeat measurements of basepower.

VIII. Calibration of ^{238}Pu Heat Standards

^{238}Pu oxide heat standards are the heat standard of choice across DOE facilities. Members of the Safeguards Science and Technology Group (NIS-5), at LANL, perform the initial and re-calibration of ^{238}Pu heat standards. Many of the ^{238}Pu heat standards have been calibrated and in use for over 20 years. The determination of the heat measurement is traceable to NIST electrical and resistance standards. For the sources with a long pedigree, the heat is usually certified to 0.05–0.1%, 95% confidence limit. The calibration certification period is usually five years.

Periodic re-calibration is necessary due to DOE Albuquerque Operations Office (ALO) calibration program order AL 57XA. Nondestructive testing is also performed on the heat standards as well as determining the heat output. The heat-standard encapsulation vessels are x-rayed to check the welds and look for container bulges due to helium buildup. A neutron/gamma dose measurement is made as well as a measurement to look for surface alpha-activity contamination. The heat source is also helium-leak checked as another verification of encapsulation integrity. The re-calibration of the heat output is necessary due to the isotopic uncertainty of the 14.3-year half-life ^{241}Pu component and the subsequent production of ^{241}Am daughter product from the beta decay of ^{241}Pu. ^{238}Pu heat standards have a nominal isotopic composition of 80% ^{238}Pu, 17% ^{239}Pu, and minor amounts of ^{241}Pu and ^{240}Pu. To minimize radiation dose, the oxygen used to make the oxide is usually enriched in ^{16}O to reduce neutron dose from ^{17}O(α, n) reactions.

The power-calibration measurements are made using heat-standards calorimeters. Heat-standards calorimeters are designed with small measurement chambers, high sensitivity, and low noise. The heat-standards calorimeters are also operated in a unique power replacement or comparison mode, which is impractical for facility use. The measurement procedure used is to make 12 power measurements on the standard being re-calibrated and 12 measurements on a heater power of the same magnitude, or a calibrated standard of nearly the same power as the standard being re-calibrated. Measurements are alternated between the comparison standard and the standard being re-calibrated until all 24 measurements are completed. The power of the heat standard being calibrated is determined using the sensitivity of the calorimeter as determined by the heater power or comparison heat standard. The measurements are made continuously using robotically controlled item manipulation. If electrical heater standards are used, the leads to the heater are in place during both measurements, electrical and ^{238}Pu.

IX. Calorimetric Assay Procedure

Calorimetric assay is most frequently used to measure plutonium-bearing items with varying amounts of ^{241}Am. The total amount of ^{241}Am is dependent on the time since separation and the fraction of plutonium that was originally ^{241}Pu. The assay procedure that will be described here will apply to plutonium items containing americium.

The baseline, BP_0, or basepower, W_0, for the calorimeter is determined first. The baseline/basepower measurement does not need to be done prior to every item measurement if the calorimeter is stable with time. The frequency of baseline/basepower measurements is normally determined by facility quality-control statisticians and is based on the observed sensor drift of the calorimeter.

After the baseline/basepower measurement is completed, the calorimeter can is removed from the measurement chamber and the item to be measured is placed in roughly the volumetric center of the calorimeter can. The void space in the calorimeter can should be filled with a conductive material. The centering and void-space filling may be omitted with a possible loss of measurement precision and or increasing bias. The magnitude of heat-distribution error and convection noise should be quantified during initial calibration if the calorimeter will be operated under non-ideal conditions. The lid is placed on the calorimeter can, and the can is placed into the measurement chamber of the calorimeter. The insulating baffle is inserted into the top of the calorimeter. The baffle must always be used and checked to be sure that the baffle top is completely down. An item measurement is initiated with the operating software.

When thermal equilibrium has been established or predicted, the software automatically terminates the calorimeter run. An additional baseline/basepower run may be taken after the item measurement if indicated by facility baseline/basepower requirements.

Passive Mode

The passive-mode thermal power is determined by solving Equation 13 for W_i. The solution to the quadratic equation when $S_0 > 0$, [MA82A] is, for k<0:

$$W_i = \frac{-S_0}{2*k} - \left[\left(\frac{-S_0}{2*k} \right)^2 - \left(\frac{BP_0 - BP_i}{k} \right) \right]^{1/2}, \qquad (15)$$

and if k>0, then W_i is

$$W_i = \frac{-S_0}{2*k} + \left[\left(\frac{-S_0}{2*k} \right)^2 - \left(\frac{BP_0 - BP_i}{k} \right) \right]^{1/2}. \qquad (16)$$

Equations 15 and 16 are specialized rearrangements of the more familiar form of the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4 *a *c}}{2 *a}. \tag{17}$$

This solution is necessary due to the rounding errors that occur using equation 17 when the product of a and c is much smaller than b squared.

Servo Mode

The calculation of item power, W_i, in servo mode is

$$W_i = W_0 - W_H \tag{18}$$

where W_0 is the control power with no item in the calorimeter, and W_H is the control power with an item in the calorimeter.

Specific Power

High-resolution gamma-ray spectroscopy measurements are usually made to determine the plutonium isotopic and ^{241}Am mass fractions; hence the effective specific power for plutonium-bearing items, using Equation 4. Sample calculations of typical effective specific powers for high- and low-burnup plutonium are shown in Table 4. The fraction of thermal power from each plutonium isotope is also listed in Table 4. It should be noted that because of the inclusion of ^{241}Am, the sum of the relative fractions is greater than one by the amount of ^{241}Am contained in the sample. The mass fraction of ^{241}Am is in terms of grams per gram plutonium. Further details on gamma-ray isotopic

Table 4: Plutonium Effective Specific Power Calculations.

Radionuclide		Ri	Pi (mW/g)		Ri*Pi (mW/g)		Power (%)
High Burnup							
Pu-238		0.0120	567.57		6.8108		58.15
Pu-239		0.6253	1.9288		1.2061		10.32
Pu-240		0.2541	7.0824		1.7996		15.40
Pu-241		0.0668	3.412		0.2279		1.95
Pu-242		0.0419	0.1159		0.0049		0.04
Am-241		0.0145	114.4		1.6588		14.13
	Total	1.0146		P_{eff}	11.6818	Total	100.00
Low Burnup							
Pu-238		0.0001	567.57		0.0327		1.47
Pu-239		0.9636	1.9288		1.8586		83.43
Pu-240		0.0356	7.0824		0.2522		11.32
Pu-241		0.0006	3.412		0.0019		0.08
Pu-242		0.0002	0.1159		0.0000		0.00
Am-241		0.0007	114.4		0.0822		3.69
	Total	1.0007		P_{eff}	2.2277	Total	100.00

measurements may be found in reference [AS1030]. The final gram quantity of the item is determined by dividing the power by the effective specific power as shown in Equation 5.

Parameters Affecting Assay Time

Calorimetry measurement times are typically longer than other NDA techniques. The packaging conditions and matrix of the item cannot change the heat output of the material, but they are usually the determining factor for measurement time. Time series data collected with a twin-bridge water-bath calorimeter operated in passive mode are presented in Figure 14. The series of lines represent different matrix conditions. The effect of matrix on measurement time is apparent in Figure 14. It can also be seen that the matrix has no effect on the magnitude of the final answer (i.e., the bridge potential at equilibrium). For each measurement presented in Figure 14, the calorimeter can, including the matrix and source, was pre-equilibrated to the same temperature before insertion into the calorimeter. Pre-equilibration was done to minimize the time response due to starting temperature variability, therefore maximizing the time sensitivity to matrix. The different matrices containing the same 1.25 W heat standard reached equilibrium in a time range of 3 to 14 hours. The matrices in order of increasing time to equilibrium were 1/2 full salt, full foil, full salt, 1/2 full copper, and full copper.

Figure 14: Graphical presentation of calorimetry matrix independence. The lines decrease in shade and increase in width with increasing time to equilibrium for clarity.
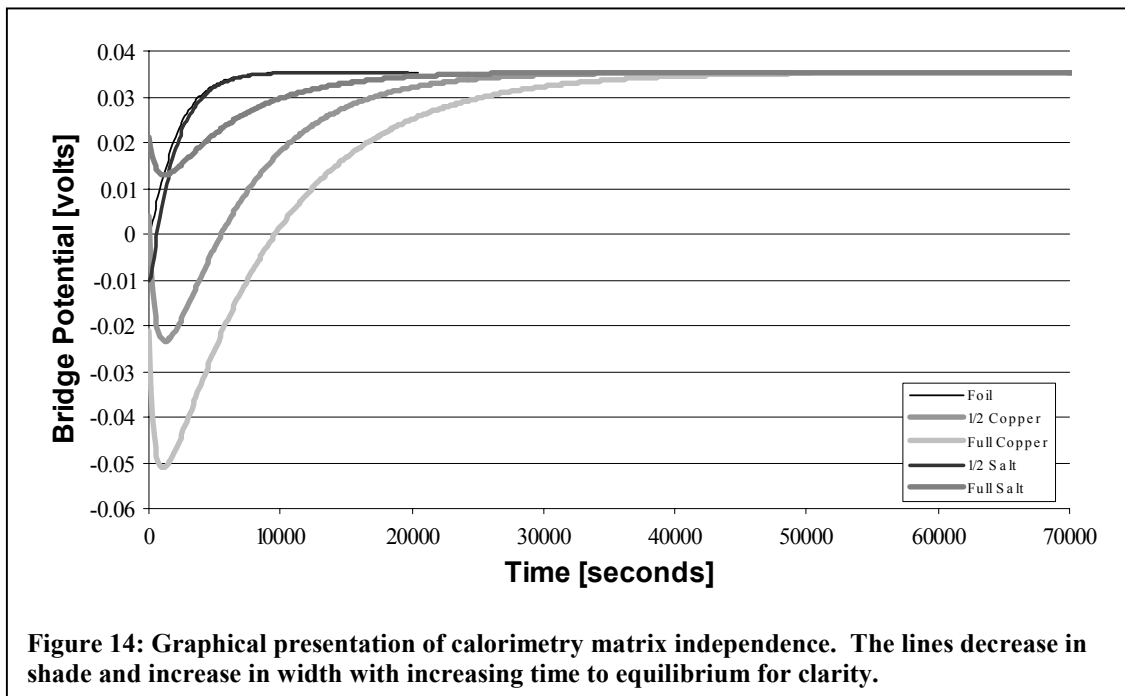
Typical assay times are between one and eight hours. Small, well-packaged thermally conductive samples can be assayed in less than one hour, while large nonconductive items, such as salts, and poorly packaged (i.e., multiple layers of air gaps and thermal insulators) can take as long as 24 hours. Pre-equilibrating the sample temperature to match the final internal calorimeter temperature can reduce the measurement time of any sample. Pre-equilibration is usually used with a calorimeter operating in servo-control

mode. An inherent benefit of the DOE/OSS-developed heat-flow calorimeters is that equilibrium prediction can also be used to reduce measurement times by 40% or more, depending on measurement conditions. The thermal diffusivity of the matrix of the item and its packaging will determine the thermal time constant for heat transfer from the item and hence the measurement time. Increases in measurement time are expected for items with large masses and small power, items that make poor thermal contact with their containers, items that contain a large amount of insulating material or dead air spaces, and items with multiple layers of containment.

The measurement time for the servo mode of operation can be shorter than for the passive mode because the calorimeter components are at the equilibrium temperature and the servo-controlled internal heater can supply heat actively to drive the item to equilibrium.

The time necessary for a calorimeter to reach thermal equilibrium during the assay of an item is dependent on a number of factors:
a) initial temperature of item relative to final equilibrium temperature of the item/calorimeter (sample preconditioning can reduce measurement time by reducing this difference),
b) type of heat-flow calorimeter used (passive or active),
c) calorimeter size and thermal properties (thermal conductivity and total heat capacity) of the fabrication materials,
d) thermal properties of the item and item packaging (usually more important than calorimeter properties),
e) size and weight of the item and the calorimeter,
f) use of an equilibrium prediction algorithm, and
g) required assay accuracy.

Measurement time data are presented in Table 5 and show the effects of matrix type on measurement time. The columns labeled "Eq. Time" list the times in hours it took the calorimeter to reach equilibrium. All of the items were pre-equilibrated to 24.0°C before insertion into the calorimeter. The initial internal calorimeter temperature was 25.0°C. Pre-equilibration was done so the matrix effects could be seen more easily. The calorimeter can had a volume of about 3 liters. The can was filled with the matrix type listed in Table 5. Measurements were made under two-power conditions: zero power and 0.8 watts of power. The size and weight of the heat standard were negligible compared to the volume of the calorimeter can, with the exception of air as the matrix. Times-to-equilibrium tracked well for both power conditions.

Possible Assay Interferences

- Interferences for calorimetry are those processes that would add or subtract thermal power from the power of the radionuclides being assayed.
- Interferences can be phase changes or endothermic or exothermic chemical reactions, such as oxidation.
- Undetected heat-generating radionuclides would add additional thermal power to the measurement.

- The accuracy of the method can be degraded for materials with inhomogeneous isotopic composition due to the increased uncertainty in the isotopic ratios.
- Room temperature variation may affect the stability of the reference temperature and increase measurement uncertainty.
- Noise in the electronics AC supply power generated by machinery may increase the measurement uncertainty.
- Energy can be lost due to high-energy gamma rays with large branching ratios.

Table 5. Item Measurement Time Dependence on Matrix Material.				
	No heat source		0.8 watt ^{238}Pu heat source	
Matrix Type	Mass (kg)	Eq. Time (hr)	Mass (kg)	Eq. Time (hr)
Air	0.668	4.8	0.766	5.0
Poly beads	1.722	25.0	1.723	18.7
Al foil (1)	0.094	6.8	0.094	5.0
Al foil (2)	0.286	6.0	0.287	5.8
Copper shot	15.820	25.3	15.824	21.5
Salt	3.102	15.0	3.358	15.0
Al bars/foil	3.636	17.0	3.636	15.0
Sand	4.580	15.0	4.580	13.8
Steel shot	13.782	27.0	13.782	30.0
Lead shot	20.738	12.5	20.739	12.5
Poly beads	1.728	20.0	-	-
Sand	4.670	16.5	-	-

X. Data Acquisition and Analysis

The simplicity of a calorimeter measurement would allow a user to manually collect the necessary data to determine the item power by visually taking the sensor readings from the display of a digital multimeter. The results could be calculated by hand following the procedures described in Section IV. In practice it is much better to have a data acquisition system display results and measurement diagnostics in real time. The data acquisition system should also calculate results and store data. These software features ultimately increase facility productivity by automatically doing tasks the operator would need to do manually. A user-friendly Windows-based data acquisition and analysis software package has been developed for calorimeter operation and is described in the following subsection.

MultiCal Data Acquisition Software

MultiCal is a calorimeter data acquisition and control software developed by the Safeguards Science and Technology Group of Los Alamos National Laboratory [BI00] with financial support from OSS and calorimeter users. MultiCal was developed for use with DOE/OSS-developed heat-flow calorimeter technology, and provides the capability to operate multiple calorimeters from one computer system, thereby reducing the need for a complete computer system for each operating calorimeter. MultiCal has a user-friendly graphical user interface (GUI), which allows real-time monitoring of critical calorimeter functions.

The software executes passive or servo modes of operation. In each of the operating modes, the operator can select the end-of-run determination as equilibration detection, equilibrium prediction, or a set elapsed time. The equilibrium detection and equilibrium predictions are based on techniques developed at EG&G Mound Laboratories [FE79] and described in more detail in the following sub-sections. At the end of the run, the results can be printed and/or logged to a data file for a permanent record.

MultiCal provides for flexible input of calorimeter configurations so users at the facilities may modify specific calorimeter parameters. The configuration menu option defines the hardware structure, analysis limits, and data collection parameters for each calorimeter module. There is a configuration module for each calorimeter that is defined in the system. The software features a set of on-screen forms; the user can specify measurement parameters and select measurement options as well as a complete on-line help menu. In passive mode, the operator can select baseline or assay measurements, and in servo mode the user can select basepower or assay measurements.

MultiCal provides functions to control the calorimeter instrument hardware and compute results using the data acquired during the requested operation. The data collection functions use a GPIB to communicate with digital multimeters and power-supply controllers. As data are read from the multimeters, it is graphically displayed on the video monitor in strip-chart format. The data are also analyzed in real time to determine when the measurement is complete.

When the calorimetric measurement is complete, a result form is displayed on the video monitor and an assay report is printed. For assay and basepower measurements, the end-of-run result is provided as a wattage value. For a baseline measurement, the result is provided as a voltage value. The type of display is selected on startup of the measurement by the operator and can be in graphical form, tabular form, or both. Numerous internal diagnostic checks automatically verify communication path functionality, instrument and hardware fault detection, and online data consistency testing. If an error is detected during the operation of MultiCal, a message is written to an onscreen dialog, with explanations of each potential error in the MultiCal User's Manual.

All of the raw data is written, along with the assay, baseline, or basepower measurement results, to a Microsoft Access® database. The measurement result data are written to ASCII-format files that can be accessed by any text editor. The environmental room-monitor data are also stored in a table in the database.

MultiCal has been installed in 13 DOE laboratories and is operating ~30 calorimeters. MultiCal has been most recently tested and validated, using the MultiCal Verification and Validation Plan, Version 3.00, May 2000, LA-UR-99-3603 [SC00], at the Rocky Flats facility as well as at the LANL Plutonium Facility. The software has received NQA-1 certification and is supported by a complete documentation set [SC00, SCBI].

Planned upgrades to the MultiCal software system include the following
a) improved database data management,
b) option for a more robust end-of-run determination algorithm,
c) ethernet communications capability, and
d) integration of an improved multi-exponential prediction algorithm (MEPA).

Equilibrium Detection

Equilibrium detection is achieved in MultiCal by binning raw data, smoothing, and then calculating the slope and standard deviation. Collected data are binned into 120-second-long intervals. The data are smoothed, using a weighted moving average of nine points based on a method given by Savitzky and Golay [SA64]. Then the smoothed data are evaluated in a moving group of ten points for which the average slope and standard deviation are calculated. When the slope and standard deviations fall below predefined values, the response is said to be at equilibrium.

The primary drawback of this method is that the end conditions must be set appropriately by the operator, requiring tedious tuning and modification of the initial parameters when operating conditions change. The nature of the algorithm also leads to a tendency to detect equilibrium early unless the parameters are tightly defined. Unfortunately, such tightly defined parameter definitions lead to long wait periods after equilibrium occurs for it to be detected. These drawbacks are the motivation to implement more robust equilibrium detection algorithms in MultiCal.

Equilibrium Prediction

Prediction is performed by estimating the calorimeter equilibrium response by analyzing data acquired prior to equilibrium. The currently available equilibrium response prediction has relied on the examination of a few points of data and the assumption that the calorimeter response can be simply modeled as a single exponential [PE88, FE79, MA87, WE97]. For example, given three data points, the expression

$$f(t) = A + B\,e^{-t/C}, \tag{19}$$

where *f(t)* is the calorimeter response as a function of time, *t*, may be solved for the values of *A*, *B*, and *C*. *A* is the equilibrium response, *B* is the magnitude of the exponential response, and *C* is the corresponding exponential time constant. Shortcomings associated with the single exponential approach and implementation led to the recent development of MEPA [SM00, SM01].

MEPA is a method that fits the calorimeter response to

$$f(t) = A + \sum_i B_i e^{-t/C_i}, \tag{20}$$

which is similar to Equation 19. The difference is the allowance for more than one exponential term and use of all available information. In fact, in the implementation of the fit, the number of exponential terms, *i*, is not determined in advance but is allowed to vary as needed to fit the data. A demonstration of the effectiveness of the fitting is shown in Figure 15. The close match between the fit and the data should be noted. In particular, the residual values are only 0.1% of the full range of the data. The quality of the fit shown is readily achieved across a wide range of calorimeter data.
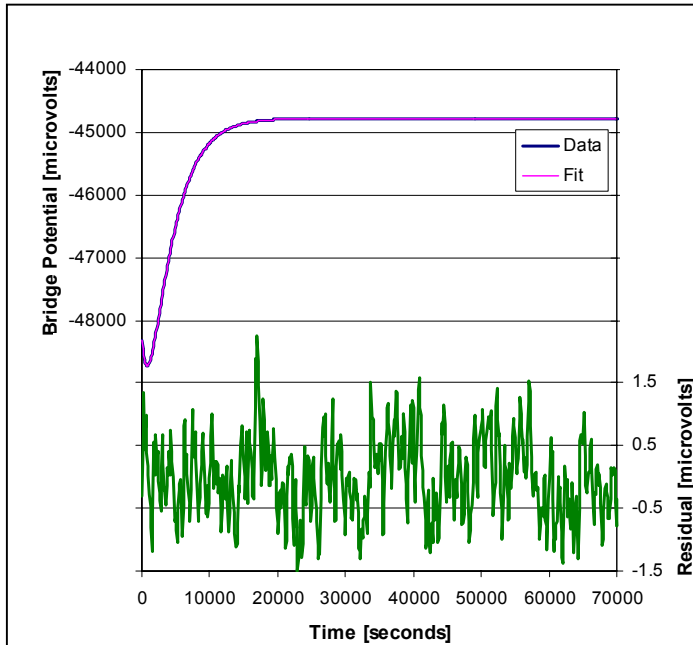
Figure 15. Top Panel: Typical MEPA fit. The fit is indistinguishable from the raw calorimeter data when viewed at this scale. Bottom Panel: Residual values from fit.

MEPA has been tested on nearly 600 calorimeter measurements. The data came from six different calorimeters operating in either servo or passive mode. One subset was taken at the DOE Rocky Flats facility; the remainder at LANL, however, three of the calorimeters tested at LANL were production models since installed in facilities. The calorimeters ranged in size from 4.0–20.3 cm diameter and were used to measure item powers up to 13 watts. The large number and variety of data sets have allowed MEPA to be fully exercised during the testing phase.

Prediction, on the above-mentioned data set, took only 49–74% of the time required for equilibrium detection. The mean deviation is an estimate of the uncertainty in the final result that should be attributed to using prediction instead of equilibrium detection. For most of the calorimeters tested, the mean deviation is of the same order as the variation seen from assay to assay when equilibrium detection is used but larger than the calorimeter precision, at equilibrium, for a single measurement. In general, MEPA requires a tradeoff between time saved and increased uncertainty. For the largest timesavings, the uncertainties increase but are still near 1% of the equilibrium value or less—comparable to other NDA techniques such as neutron or gamma measurements—and they would be acceptable for most applications [AS1207, HY99, LE00].

MEPA has been shown to accurately estimate calorimeter equilibrium response and uncertainty prior to equilibrium. The associated uncertainties in the predicted values are statistically reasonable. The selection of a particular criteria set in a facility application would be determined by the needs of the facility and the behavior of the particular calorimeter to be used. If a facility can afford some loss of precision in the results, substantial timesavings can be obtained. Any application that requires the minimum uncertainty in the results should be run to equilibrium. Work has been completed to incorporate MEPA into MultiCal to make the prediction method widely available to calorimetry users.

Assay Error Determination

Mixed Radionuclides (plutonium and ^{241}Am mass)

The mass, M, of plutonium in an item is the total power, W, divided by the effective specific power, P_{eff}, of the item. The measurement of these two quantities is independent so the relative uncertainty for the plutonium mass, M, can be written as

$$\frac{\sigma_M}{M} = \left[\frac{\sigma_W^2}{W^2} + \frac{\sigma_{P_{eff}}^2}{P_{eff}^2} \right]^{1/2}. \tag{21}$$

The uncertainty in the power measurement, σ_W, can be obtained from replicate power measurements of heat standards or from historical data. It should include both precision and bias components. The uncertainty in P_{eff}, $\sigma_{P_{eff}}$, comes from the uncertainty in the isotopic fractions, R_i, and isotopic specific powers, P_i. The uncertainties in the isotopic fractions are determined from uncertainties in the various techniques that might be used for the isotopic analysis, such as mass spectroscopy, alpha counting, or gamma-ray spectroscopy. There are sufficient gamma rays in plutonium to provide independent measured isotopic ratios of the major contributors to the item thermal power: ^{238}Pu, ^{240}Pu, and ^{241}Pu with respect to ^{239}Pu, and ^{241}Am with respect to total plutonium that allow R_i to be calculated. The mass fraction of ^{242}Pu, usually a minor contributor to the thermal power, is determined by isotopic correlation using the other plutonium isotopic data. The correlation technique is necessary due to the absence of gamma rays from ^{242}Pu. The uncertainties in the isotopic specific powers, P_i, as determined by different experiments, are given in Table 2. The test method for determining isotopic composition by gamma-

ray spectroscopy is described in "C1030 Standard Test Method for Determination of Plutonium Isotopic Composition by Gamma-Ray Spectrometry" [AS1030]. Several commercially available gamma-ray analysis codes not only provide the isotopic composition but also the uncertainties of the isotopic fractions and the specific power of the item being measured. Error propagation of the isotopic fractions is discussed in Reference [SA83].

The uncertainty of the ^{241}Am mass mixed with plutonium is

$$\frac{\sigma_M}{M} = \left\{ \left(\frac{\sigma_W}{W} \right)^2 + \left(\frac{K}{P_{eff}} \right)^2 \left[\left(\frac{\sigma_K}{K} \right)^2 + \left(\frac{\sigma_{R_{Am}}}{R_{Am}} \right)^2 \right] + \left(\frac{R_{Am}\sigma_{P_{Am}}}{P_{eff}} \right)^2 \right\}^{1/2}$$ (22)

where

$$K = P_{eff} - P_{Am} R_{Am}$$ (23)

where P_{Am} is the specific power of ^{241}Am, R_{Am} is the mass ratio of ^{241}Am to plutonium, W is the thermal power, and σ_x are the respective uncertainties [AS1458].

Single Radionuclide (Tritium)

The uncertainty of a calorimetric assay of tritium can be calculated using Equation 25.

The uncertainty of the effective specific power, P_{eff}, of tritium is the same as the isotopic specific power; 0.00045 Watt [RU77]. Dividing by the specific power of tritium, 0.3240 W/g, results in

$$\frac{\sigma_{P_{eff}}}{P_{eff}} = 0.0014 .$$ (24)

So for tritium, the relative uncertainty of the tritium mass is

$$\frac{\sigma_{tritium}}{M_{tritium}} = \left[\left(\frac{\sigma_W}{W} \right)^2 + (0.0014)^2 \right]^{1/2} .$$ (25)

For any item containing a single radionuclide, the contribution to the uncertainty due to the isotopic composition determination is dependent only on the specific power, P, for that isotope and the uncertainty on W.

Measurement Control

Measurement control procedures are similar for all calorimeter measurements. Replicate measurements of ^{238}Pu or electrical heat standards are performed to demonstrate that the calorimeter system, hardware, and software, are operating correctly. Other well characterized nuclear materials may be used as heat standards. The frequency of measurement control heat and baseline/basepower measurements are usually based on facility requirements that are dependent on one or more of the following:

a) performance history of the calorimeter,
b) assay precision required,

c) type of measurements being made (confirmation, material control and accounting (MC&A), shipper/receiver…),
d) location of the calorimeter (high traffic, other equipment…),
e) environmental conditions (temperature fluctuations, external air…),
f) size of items,
g) range of power measurements,
h) throughput per day,
i) whether it is a portable or permanent system, and
j) data collection systems used.

Corrections to the thermal power of radioactive heat standards due to radioactive decay are made to compare measurements made on different dates. Data collected from a measurement control program can be used to calculate the precision and bias of the power measurement.

Control charts formed from replicate measurements of heat standards must be used to provide quantitative means for determining that the calorimeter system is operating satisfactorily prior to a single measurement or group of measurements. In addition, these charts can be used to demonstrate that the calorimeter was in control during the assay runs. Control charts may also be used on baseline/basepower measurements to provide auxiliary information in case abnormal operating conditions are detected.

Calorimeter bath temperatures can be monitored continuously to flag changes that will affect calorimeter performance. The temperatures may be evaluated using control charts or administrative limits.

More details on measurement control may be found in references [ANN15.54, AS1009, ANN15.20].
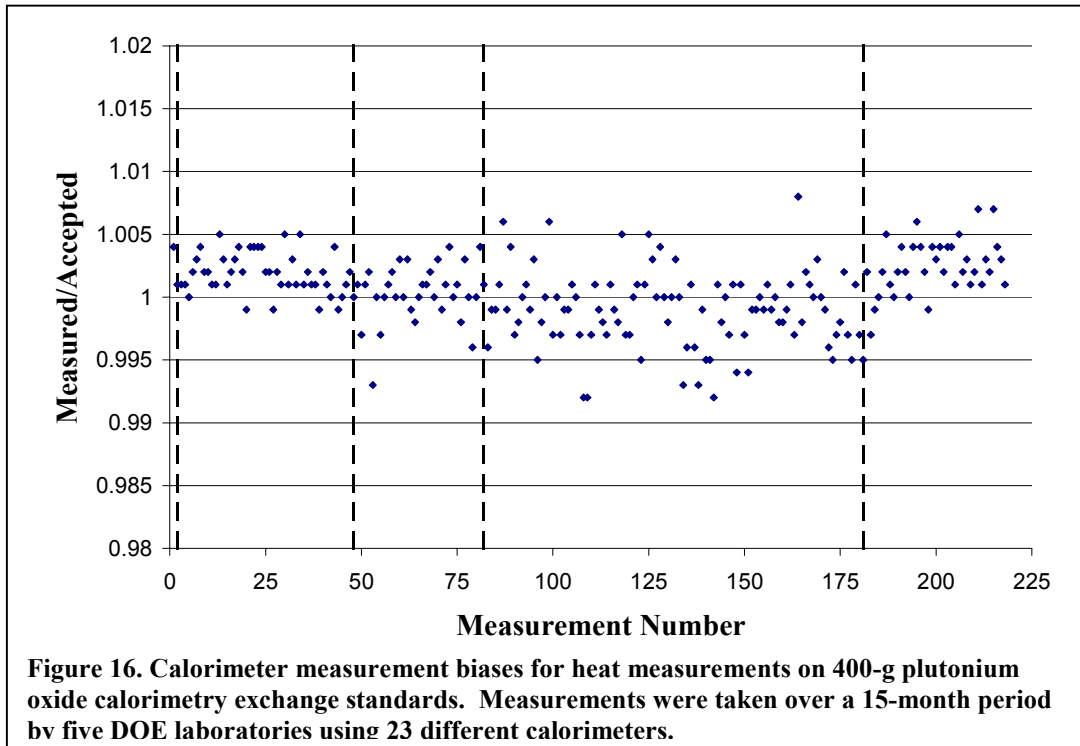
XI. Measurement Performance

The accuracy and reliability of calorimetric assay are primarily dependent on the thermal power generated by the item and on the methods used to determine P_{eff}. The total measurement uncertainty on P_{eff} determined for pure homogeneous items using gamma-ray spectroscopy is comparable to the power measurement uncertainty [SA99]. For materials containing reasonable concentrations of plutonium (>100g Pu/liter), the precision and bias of calorimetric assay are comparable to good chemical assay techniques [WE95]. In this case, the largest source of calorimetry error is due to the uncertainty of the specific powers, P_i, of the individual radionuclides.

For impure or heterogeneous items, calorimetric assay can have lower uncertainties than destructive analysis techniques [WE95A] because of destructive analysis sampling error. The power measurement integrates all of the heat produced by the item regardless of inhomogeneity and for heterogeneous items the determination of P_{eff} by gamma-ray spectroscopy is a more representative average of the entire item than destructive analysis. In this case, where the isotopic composition of the plutonium is determined by gamma-ray spectroscopy the final uncertainty in the gram value determined by calorimetric assay is dominated by the uncertainty of the mass fractions, R_i, in P_{eff}.

The precision and bias of calorimeters used for plutonium measurements vary with the thermal power of the item being assayed and are dependent in part on the calorimeter size. Over two hundred heat-flow calorimeters developed under the DOE/OSS Technology Development Program have been built for use throughout the DOE complex and the world over the last 50 years. Nearly 60 calorimeters are in use at DOE facilities across the country. Calorimeter biases for 23 of these calorimeters at 5 DOE facilities are presented in Figure 16. The dashed vertical lines separate the data submitted by each laboratory. These data were collected for the calorimetry exchange program over a 15-month period starting in October 1993. The power of the calorimetry exchange standard was 1 W during this time period. All measurements have a bias of less than ±0.8%. The average bias is 1.0004 with a standard deviation of the average of ±0.0002. The error expected on a single measurement would be 0.3% 1RSD.

Calorimetric assay is considered the "gold standard" of NDA measurements for items containing more than 0.5 kg of plutonium of any form in a container less than 10 inches in diameter. Since calorimetry can measure entire items with very high precision and low bias, the results are often comparable to DA measurements. Calorimetry is frequently used as a standard measurement to determine uncertainties and/or biases in other NDA techniques such as neutron counters [AS1207] and tomographic gamma scanner (TGS) systems [HY99, LE00]. Quantitative examples of the measurement precision and bias obtainable using calorimetric assay are presented in the following sub-sections.

Figure 16. Calorimeter measurement biases for heat measurements on 400-g plutonium oxide calorimetry exchange standards. Measurements were taken over a 15-month period by five DOE laboratories using 23 different calorimeters.

Assay Precision and Bias

Calorimetric assay of items containing multiple radionuclides requires calorimetry and isotopic analysis. The precision and bias of the calorimetric assay of multi-radionuclide items will have components due to uncertainties in P_{eff} and power. For single radionuclide items, the uncertainties will be due only to the power measurement and the specific power of the radionuclide. The precision of a calorimeter measurement is dependent on the sensitivity of the calorimeter, baseline stability, and item power.

Some major factors that can affect the precision of P_{eff} determined by gamma-ray isotopic assay include [AS1030]:
a) count rate,
b) count time,
c) absorbers,
d) sample geometry,
e) sample mass,
f) sample isotopic composition, and
g) instrument stability.

Bias corrections to isotopic ratios determined by gamma-ray spectroscopy are made to account for biases in the branching ratios, half-lives, peak areas, and relative efficiency curves if shown to be necessary by comparison with isotopic standards.

Some major factors that can affect the bias of P_{eff} determined by mass spectrometric methods include [AS697]:

a) mass spectrometric analytical error,
b) ratio of the isotopes,
c) possible systematic error in the composition of separated isotopes used for calibration, and
d) possible systematic error in chemical analysis.

Data collected from a measurement control program can be used to calculate the precision and bias of the power measurement. A summary of the precision and bias of the power measurement obtained from replicate measurements of ^{238}Pu heat standards in production facilities over a 0.5—1.0 year period is shown in Table 6.

Table 6. Calorimeter Power Measurement Precision and Bias					
Heat standard Power, Watts	Calorimeter diameter, m	Calorimeter Type, operation mode	Number of Meas.	Precision, % RSD	Bias, %
98.0	0.06	rod, servo	29	0.065	0.02
3.5	0.15	rod, servo	55	0.09	0.00
4.0	0.25	twin, passive[1]	22	0.05	0.03
4.9	0.30	twin, passive[1]	34	0.06	0.05
0.0786	0.04	Solid state, passive[2]	10	0.23	0.001

[1]Pooled results from two calorimeters.
[2]Measurements made in laboratory.

Calorimetric Assay Precision and Bias Data

Plutonium in PuO$_2$-UO$_2$ Mixed Oxide

Generally, the greater the thermal power of an item in a calorimeter, the better the relative precision. To illustrate this relationship, the precision observed from repetitive calorimeter measurements of six items containing 26 to 258 grams of Pu (17% ^{240}Pu) in PuO$_2$-UO$_2$ (26% Pu) was calculated; the results are shown in Table 7 [RU00]. These measurements were made over a 56-day period with a water-bath twin-bridge over-under calorimeter. The items were loaded robotically, allowing for continuous operation. A common P_{eff} factor for all six items was determined using the plutonium isotopic composition and ^{241}Am content that was determined by mass spectrometry and alpha counting. The calorimeter can size was 6.4 cm diameter x 16.5 cm high. The calorimeter measurement time was fixed at 1 hour. The calorimeter was run in the servo mode, and the items were preconditioned to reduce measurement time. The high precision results listed in Table 7 are direct evidence that automated loading and unloading of items into the calorimeter can improve measurement precision.

Table 7. Automated Plutonium Assay System Measurement Results[1]						
ID	Mass[1,2], g by Chem	Mass[2], g by Cal[3]/MS/α[4]	Precision[5], g	Precision, % RSD	Bias, g	Bias, %
4	257.70	257.54	0.14	0.06	-0.16	-0.06
5	206.09	206.06	0.13	0.06	-0.03	-0.02
6	206.18	206.12	0.14	0.07	-0.06	-0.03
7	128.81	128.94	0.12	0.09	0.13	0.10
8	77.28	77.35	0.12	0.15	0.07	0.09
9	25.79	25.99	0.11	0.42	0.20	0.78

[1] Mass of plutonium determined by coulometry using reference material NBS 949E. Plutonium percentage of mixed oxide, 0.25759, based on triplicate measurements of 6 samples.

[2] Plutonium masses reported here decayed to a common date.

[3] Final results based on 117 replicate calorimeter measurements per item.

[4] Isotopic composition determined by 12 replicate measurements by mass spectrometry (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and 6 replicate alpha-counting (^{238}Pu, ^{241}Am) measurements. Average Pu isotopic and ^{241}Am results were used to calculate P_{eff}.

[5] Precision due to calorimetry power replicate measurements.

Plutonium in PuO$_2$

The results of multiple calorimetry and gamma-ray isotopic measurements by three facilities on identical standards, each containing 400 grams of well characterized plutonium (6% ^{240}Pu) in PuO$_2$, are shown in Table 8 [SP99]. The plutonium content and isotopic composition used as reference values of the mother lot of PuO$_2$ material used for these standards were measured by coulometry and mass spectrometry/alpha counting by 4 analytical labs. The calorimetry and gamma-ray measurements used to determine plutonium mass variabilities and biases reported in Table 8 were taken over a one-year period. The within-facility variability and the bias of the calorimetric/gamma-ray assay were calculated from results reported by each facility decayed to a common date. Each facility used different gamma-ray analysis codes for the isotopic measurements. For some, the reported values are the averages of measurements of the standard item with different calorimeters.

Table 8. Calorimetry/Gamma-Ray Assay Measurement of 400 Grams of plutonium in PuO$_2$[1]				
Facility	Within-Facility Variability, g	Within-Facility Variability, % RSD	Bias, g	Bias, % RSD
A[2]	1.5	0.38	0.03	0.01
B[2]	1.5	0.38	-0.40	-0.10
C[3]	1.4	0.36	0.04	0.01

[1] All masses are in grams of plutonium decayed to a common date.

[2] Measurements made using multiple water-bath twin-bridge calorimeters.

[3] Measurements made using "air-bath" calorimeter.

Calorimetric Assay Bias Data

The bias of calorimetric assay can be determined by the measurement of certified reference materials or well characterized items with known elemental and isotopic

compositions. Biases for calorimetric assay of plutonium in PuO_2-UO_2 mixed-oxide powder and plutonium in PuO_2 powder have been previously shown in Tables 7 and 8, respectively. These data show that the biases for this measurement application are typically less than 0.1% and are also typically less than the within-facility variability.

Power and P_{eff} Precision and Bias Data

The DOE Calorimetry Exchange Program tabulates the results from the facility's measurements of a standard PuO_2 sample containing 400 g of plutonium with about 6% [240]Pu content. Each facility collects data in a manner suitable for its own operations. DOE calorimetry exchange data taken at five different DOE facilities is presented in Table 9. The data were collected over an 8-year period from 1990 to 1998. Not all facilities reported results each year. Therefore, the averages contained data from a maximum of 8 years and a minimum of 5 years. Presented in Table 9 are the average percent measurement bias and percent relative standard deviation (RSD) from repeated measurements for P_{eff} and item power. The plutonium oxide exchange standard has a nominal power output of 1 watt and is 5.86% [240]Pu by weight total plutonium. The percent bias and percent RSD are comparable for power and P_{eff} measurements on this item.

Table 9. Calorimetry Exchange Precision and Bias Data for P_{eff} and Power				
Facility	Power		P_{eff}	
	% Bias[1]	% RSD[2]	% Bias[1]	% RSD[2]
A	0.11	0.61	-0.23	0.10
B	0.08	0.22	0.07	0.26
C	-0.01	0.17	0.13	0.21
D	-0.08	0.30	0.02	0.20
E	0.17	0.21	-0.18	0.48

[1]% Measurement Bias = 100*[Measured – Accepted)/Accepted].
[2]% Relative Standard Deviation is based on repeated measurement of the same item.

Plutonium in Salt Residues

In two separate studies calorimetry and gamma-ray spectroscopy measurements were used to assay items containing a mixture of KCl, $MgCl_2$, and NaCl residues containing $PuCl_3$ and $AmCl_3$ as well as shards of MgO crucibles and plutonium metal shot [LO90, FL86]. After the above measurements were performed, the material was then crushed, sampled, and analyzed chemically for plutonium, using isotopic dilution mass spectroscopy (IDMS). The Pu content of the items ranged from 55 to 416 g. The average relative bias between the calorimetric assay and the chemistry is shown in Table 10. A twin-bridge water-bath calorimeter was used for the measurements. These biases are dominated by the difficulty in determining P_{eff} due to the isotopic heterogeneity of the items.

Table 10. Calorimetry/Isotopic Measurements of Pu and Am in Molten Salt Residues					
Mass Range, g Pu	No. of Items	Mass Range, g Am	Bias, % Pu	Bias, % Am	References
35-416	10	0.4-18	1.5±0.5[1]	0.2±0.4[A]	51
214-414	9	5-26	1.6±0.6[2]	0.2±0.6[B]	52

[1] Chemistry–Pu and Am elemental analysis by isotopic dilution mass spectrometry. Aliquots taken of blended salt matrix for analysis. Pieces of Pu metal removed, oxidized, and returned to matrix before blending.
 Calorimetry–Isotopic analysis for P_{eff} determination by gamma-ray spectroscopy.
[2] Chemistry–Entire matrix of each item dissolved and liquid samples measured by x-ray fluorescence for Pu and gamma counting for Am.
 Calorimetry–Isotopic analysis for P_{eff} determination by gamma-ray spectroscopy and facility stream averages of certain Pu isotopic ratios.

Am in Salt Residues

The same measurement systems described above were used to assay the [241]Am content of the items containing molten salt residues as well as the Pu content [LO90, FL86]. Gamma-ray spectroscopy was used to determine the [241]Am/Pu ratio simultaneously with plutonium isotopic ratios. IDMS was also used to determine the Am content of the crushed material. The Am content of the items ranged from 0.4 to 18.4 g. The relative mean bias for the calorimetric assay compared to the chemistry is presented in Table 10.

Tritium

Calorimetry was used to measure the quantity of tritium gas in containers. Since tritium was the only radioactive isotope, no isotopic measurements were required for the assays. After the calorimeter measurement, the gas was quantitatively transferred to tanks with calibrated volumes, and the quantity of tritium was determined using calibrated pressure and temperature transducers and mass spectrometric analyses. A comparison of measurement results between calorimetry and pressure/temperature measurements in a calibrated volume combined with mass spectrometric analysis (PVT/MS) was made for 50 containers [LI87]. The tritium content of the containers ranged from 15 to 16 g. The relative mean bias for the calorimetric assay compared to PVT/MS was -0.12%. One RSD of the mean was 0.05%. A twin-bridge water-bath calorimeter was used for the calorimeter measurements.

IAEA Cal/ DA Comparison

In 1994, the International Atomic Energy Agency (IAEA) initiated nuclear materials safeguards on plutonium-bearing oxide and scrap items at Hanford. Due to the widely ranging chemical purities and the heterogeneous nature of the scrap items, 17 items were selected for detailed measurement analysis using a range of destructive and nondestructive analysis techniques. Measurements were made by multiple entities such as the facility operator (Westinghouse Hanford Company), the state system (USDOE), the IAEA, and LANL. A subset of the complete measurement campaign is presented in Table 11 [WE95A], including 5 items each from the PD and SC stratum items. The PD items consisted of purer PuO_2 items; the SC items were considered scrap by the IAEA.

Presented in Table 11 are the facility DA and calorimetric assay results, IAEA DA results, and results from the LANL 3 ring multiplicity counter (3RMC). Of the four analysis techniques listed in Table 11, calorimetry has the lowest overall measurement bias compared to the declared and shipper values, ranging from 0.2% to 0.5%. The two DA techniques are in good agreement with the shipper values and calorimetric assay for the PD stratum items, but the DA techniques show larger bias variability on the SC scrap items. The 3RMC made reliable measurements on the PD items but showed large biases for the SC items.

The conclusions made by Welsh et al. [WE95A], based on the complete data set, was that the difficulty, exposure, expense, and unknown interferences of destructive analyses, along with the demonstrated accuracy of calorimetry, warrants the IAEA's investigation of using calorimetry for verification purposes, especially for scrap. The 3RMC was found to be satisfactory for verifying PD stratum items and superior to calorimetry in measurement time, 30 minutes in the 3RMC relative to the 6-hour calorimeter measurement time. For the highly impure scrap items, the 3RMC required longer measurement times than the calorimeter, with widely variable bias results ranging from 2.3% to –40.4%.

Table 11. Hanford/IAEA Measurement Bias Results.					
Item ID	Pu mass (g)	% Relative difference from declared or shipper values[1]			
	Shipper value[2]	DA CA[3]	CAL[4]	IAEA DA[5]	3RMC[6]
PD1	271	0.4	0.0	0.4	1.8
PD2	476	0.0	0.0	-0.2	0.6
PD3	870	-0.1	0.2	0.0	0.5
PD4	869	-0.2	0.1	-0.1	-0.2
PD5	873	0.0	0.2	0.2	0.3
	Declared[7]				
SC1	268	-0.8	-0.4	-3.1	7.5
SC2	389	-0.5	-0.5	0.0	-8.0
SC3	468	-4.1	0.4	-0.4	-40.4
SC4	908	-2.8	-0.2	1.2	-2.3
SC5	1710	-0.3	-0.2	2.5	-7.3

[1]% Relative Difference = [(Accepted – Measured)/Declared]*100.
[2]Gram quantities assigned to items based on shipper values.
[3]Hanford destructive analysis using amperometric titration [AS698].
[4]Hanford calorimetric assay using NDA gamma-ray determination of P_{eff}.
[5]IAEA destructive analysis using Macdonald and Savage technique [MA78].
[6]Results determined by LANL/IAEA using the 3-ring multiplicity neutron counter.
[7]Gram quantities assigned to items based on facility declarations.

An additional detailed evaluation by Hanford, IAEA, and LANL of random and systematic uncertainties associated with destructive analysis (DA) and NDA of two types of materials designated "pure" plutonium dioxide and scrap plutonium dioxide at the Hanford Plutonium Finishing Plant (PFP) was made [WE95]. The random and systematic uncertainties associated with using DA determined by Welsh et al. [WE95] are presented in Table 12. The random and systematic uncertainties determined based on measurement

experience at Hanford associated with using calorimetric assay, High Level Neutron Counter (HLNC) and the 3RMC are also listed. Included in Table 12 are the random and systematic uncertainties expected for the material types based on IAEA measurement experience.

One of the conclusions in the Welsh et al. study was the variability of calorimetric assay was comparable with, or superior to, the variability of the DA due to the significant sampling variability associated with the DA aliquots.

Table 12. Random and Systematic Measurement Variability Estimates in Percent				
Measurement Type	PFP Experience Random/Systematic		IAEA Experience Random/Systematic	
	"Pure" PuO_2	PuO_2 Scrap	"Pure" PuO_2	MOX Scrap
DA Titration	0.2/0.1	2.6/0.1	0.2/0.1	~3/~1.5
DA Solution Counter	0.8/0.2	1.5/0.2	--/--	--/--
Calorimetric Assay	0.34/0.1	0.64/0.1	--/--	--/--
HLNC	~3/--	~10/--	~1/~0.8	~8/~3
3RMC	~2/--	~8/--	--/--	--/--

XII. Commercially Available Calorimeters

There are three sources of commercially produced calorimeter systems designed exclusively for the measurement of radioactive material. An "Air Bath" calorimeter design described previously is available from Antech Corporation, a rod calorimeter design can be purchased from Canberra Industries, and a solid-state calorimeter from International Thermal Instrument Company. Wheatstone bridge water-bath calorimeters, described in Section IV, are not currently commercially produced, but design packages are available for use by DOE facilities.

Contacts:

Canberra Industries, Inc.	Antech Corporation	International Thermal
800 Research Parkway	Unit3, Thames Park	Instrument Company
Meriden, CT 06450	Lester Way, Wallingford	P.O. Box 309
203-639-2256	Oxfordshirne OX10 9TB, UK	Del Mar, CA 92014
	US: 303-430-8184	858-755-4436

XIII. LANL Calorimetry Program Capabilities and Services

The current DOE/OSS-developed, high-precision heat-flow calorimeter technology is available for transfer to commercial vendors. MultiCal, a Windows®-based calorimeter data acquisition and control system, is available for use with heat-flow calorimeters. The Safeguards Science and Technology Group at LANL will continue to improve measurement systems and produce instruments for custom applications. Calorimeter procurement costs vary with instrument size, sensitivity, measurement precision, and level of custom design effort and are comparable to other NDA instrumentation costs.

Los Alamos offers continuing support for existing calorimeters. We can also participate in acceptance testing, NIST-traceable calibration of ^{238}Pu heat standards, calibration of measurement systems using nuclear material, and implementation of software and hardware upgrades to existing systems.

XIV. Training

Two courses related to calorimetry are offered under the Safeguards Technology Training Program, sponsored through the US DOE Central Training Academy. The courses are Calorimetric Assay School (MCA-244) and a Calorimeter Operator Training School (MCA-246). The Calorimetric Assay School is usually presented at LANL; the Calorimeter Operator Training School is usually presented at the requesting facility.

The Calorimetric Assay School is offered annually and provides a comprehensive overview of the theory and application of calorimetric assay to plutonium- and tritium-bearing materials. Lectures and laboratory exercises provide personalized instruction and hands-on experience. Topics include principles and applications of heat-flow calorimeters for determining the thermal power emitted from plutonium and tritium, high-resolution gamma-ray measurements for calculating isotopic composition and specific power, conversions of measured thermal power into an assay result, increasing calorimeter throughput, and considerations of heat standards and measurement control. Activities involve the use of radioactive materials.

This course is designed for DOE employees, contractors, and facility personnel who are involved in the measurement and accounting of nuclear materials. This course is of interest to professionals who operate calorimeters, manage calorimeter operations, or evaluate calorimetry measurements for nuclear material accountability. Employees of other organizations are accepted on a space-available basis.

The Calorimeter Operator Training School is offered upon request for all interested parties. This course is usually given at the facility making the request for training. The emphasis is on operation of the actual calorimeters used at the facility. The skills and procedures necessary to perform good calorimetry measurements are covered in detail. No time is spent on the associated isotopic composition measurement. The course is customized to meet the needs of the facility requesting training and focuses on the type of heat-flow calorimeters being used at the facility.

For more information contact:
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                                       e-mail: phypes@lanl.gov

Safeguards Science and
Technology (NIS-5) Group Office: Phone: 505-667-6141

XV. Summary of Current Calorimeter Research Projects

Hardware and software solutions are being developed to reduce calorimeter measurement times, increase precision and accuracy, reduce fabrication costs, reduce fabrication time, decrease calorimeter size, apply calorimetry to waste measurements, increase portability, decrease instrument down time, and develop more robust instruments.

Projects are in the areas of
- Software development [SM00, SM01, BI00]
- Solid-State sensors [BR00, BR98, BR97]
- Fiber Optic sensors [RU98, RU98A, DA98]
- Low-Wattage Electrical Calibration Heater (LWECH) [BI97]
- Calorimeter waste measurements [RU00A, RU00B]
- Combined calorimetry and neutron measurements [RU99, RU99A]
- Measurements of highly enriched uranium [RU99, RU99A, RU97]
- Transparency measurements using heat signatures [BR99]
- Calorimeter equilibrium prediction [FE79, PE88, MA87, WE97, SM00, SM01]
- Heat flow modeling [RA01, SM01A]

XVI. List of Abbreviations and Acronyms

3RMC   Three-ring neutron multiplicity counter

ALO   Albuquerque Operations Office

ANM   Alternative Nuclear Material

ANSI   American National Standards Institute

ASTM   American Society for Testing and Materials

DA   Destructive Analysis

D/A   Digital-to-Analog

DOE   Department of Energy

GPIB   General Purpose Interface Bus

GUI   Graphical User Interface

HDE   Heat Distribution Error

HLNC   High Level Neutron Counter

hr   Hour

IAEA   International Atomic Energy Agency

IDMS   Isotopic Dilution Mass Spectroscopy

kg   Kilogram

LANL   Los Alamos National Laboratory

LLNL   Lawrence Livermore National Laboratory

LWECH   Low Wattage Electrical Calibration Heater

MASS   Material Accounting and Safeguards System

MC&A   Material Control and Accounting

MEPA   Multi-Exponential Prediction Algorithm

MeV	Million Electron Volts
NDA	Nondestructive Assay
NIS-5	Safeguards Science and Technology Group, Nonproliferation and International Security Division, Los Alamos National Laboratory
NIST	National Institute of Standards and Technology
OSS	Office of Safeguards and Security
PD	IAEA stratum classification of items as purer PuO_2
PFP	Plutonium Finishing Plant
PVT/MS	Pressure/Temperature measurements in a calibrated Volume combined with Mass Spectrometric analysis
RSD	Relative Standard Deviation
SC	IAEA stratum classification of items as scrap
SNM	Special Nuclear Material
TGS	Tomographic Gamma Scanner
TRU	Transuranic
SNM	Special Nuclear Material
USDOE	United States Department of Energy
W	Watt

XVII. References

[ANN104]   Methods for Chemical, Mass Spectrometric, and Spectrochemical
            Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets, ANSI
            N104-1973 (American National Standards Institute, Inc., New York,
            1973).

[ANN572]   Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear,
            and Radiochemical Analysis of Nuclear-Grade Plutonium Metal, ANSI
            N572-1974 (American National Standards Institute, Inc., New York,
            1974).

[ANN15.20] American National Standard Guide to Calibrating Nondestructive Assay
            Systems, ANSI N15.20.

[ANN15.22] American National Standard for Nuclear Materials - Plutonium-Bearing
            Solids Calibration Techniques for Calorimetric Assay, ANSI N15.22-
            1987.

[ANN15.54] American National Standard for Instrumentation – Radiometric
            Calorimeters – Measurement Control Program, ANSI N15.54.

[AS697]   Standard Test Method for Chemical, Mass Spectrometric, and
            Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders
            and Pellets, ASTM Standard C 697, Sections 139-147.

[AS697A]   Standard Test Method for Chemical, Mass Spectrometric, and
            Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders
            and Pellets, ASTM Standard C 1458-00, Sections 121-128.

[AS698]   Standard Test Method for Chemical, Mass Spectrometric, and
            Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O_2),
            ASTM Standard C 698.

[AS1009]   Standard Guide for Establishing a Quality Assurance Program for
            Analytical Chemistry Laboratories Within the Nuclear Industry, ASTM
            Standard C 1009.

[AS1030]   Standard Test Method for Determination of Plutonium Isotopic
            Composition by Gamma-Ray Spectrometry, ASTM Standard C 1030.

[AS1207]   Standard Test Method for Nondestructive Assay of Plutonium in Scrap
            and Waste by Passive Neutron Coincidence Counting, ASTM Standard C
            1207.

[AS1458] Standard Test Method for Nondestructive Assay of Plutonium, Tritium, and 241Am by Calorimetric Assay, ASTM Standard C 1458.

[BE84] R. J. Beckman, S. F. Marsh, R. M. Abernathy, and J. E. Rein, "Plutonium-240 Half-Life Determined by Isotope-Dilution Mass Spectrometric Measurement of the Grown-in Uranium-236", *International Journal of Applied Radiation and Isotopes*, **35**, 163-169 (1984).

[BI97] R. Biddle, J. R. Wetzel, and R. Cech, "Design and Performance of Low-Wattage Electrical Heater Probe," Proceedings of the 38th Annual Meeting of the Institute of Nuclear Materials Management, Phoenix, AZ, July (1997).

[BI00] R. S. Biddle and C. M. Schneider, "MultiCal – Software System for Calorimeter Control," Proceedings of the Institute of Nuclear Materials Management 41st Annual Meeting, New Orleans, LA, July 17-20, 2000.

[BR97] D. S. Bracken, R. Biddle and R. Cech, "Design and Performance of a Vacuum-Bottle Solid-State Calorimeter," Proceedings of the 38th Annual Meeting of the Institute of Nuclear Materials Management, Phoenix, AZ, July (1997).

[BR98] D. S. Bracken, R. Biddle, and C. Rudy, "Performance Evaluation of a Commercially Available Heat Flow Calorimeter and Applicability Assessment for Safeguarding Special Nuclear Materials," Proceedings of the 39th Annual Meeting of the Institute of Nuclear Materials Management, Naples, FL, July (1998).

[BR99] D. S. Bracken, C. R. Rudy, B. S. Cordova, and R. S. Biddle, "Use of Solid-State Heat-Flow Sensors for Transparency Measurements," Proceedings of the 40th Annual Meeting of the Institute of Nuclear Materials Management, Phoenix, AZ, July (1999).

[BR00] D. S. Bracken and P. Hypes, "Solid-State Calorimeter," Proceedings of the 41st Annual Meeting of the Institute of Nuclear Materials Management, New Orleans, LA, July (2000).

[DA98] P. G. Davis and I. J. Bush, "Fiber Optic Calorimeter," Fourth Pacific Northwest Fiber Optic Sensor Workshop, Troutdale, OR, May (1998), SPIE Vol 3489.

[DE81] P. DeBievre, "Isotope Dilution Mass Spectrometry: Some Present Limitations and Possibilities to Overcome These," Minutes of SALE program participants meeting, July (1981) 188-207.

[EI54]   J. F. Eichelberger, K. C. Jordan, S. R. Orr, and J. R. Parks, "Calorimetric Determination of the Half-Life of Polonium-210," *Physical Review* **96**, 719 (1954).

[FE79]   C. L. Fellers and P. W. Seabaugh, "Real-Time Prediction of Calorimeter Equilibrium," *Nuclear Instruments and Methods* **163**, 499 (1979).

[FL86]   J. G. Fleissner and M. W. Hume, Comparison of Destructive and Nondestructive Assay of Heterogeneous Salt Residues, RFP-3876, 1986.

[GA80]   E. L. Garner, L. A. Machlan, "Mass Spectrometric Measurements to Determine the Half-Life of ^{241}Pu," NBS Special Publication 582, *National Bureau of Standards*, 1980, June, pp. 34-40.

[GU64]   S. R. Gunn, Radiometric Calorimetry: A Review, *Nuclear Instruments and Methods* **29**, 1 (1964).

[GU70]   S. R. Gunn, Radiometric Calorimetry: A Review (1970 supplement) *Nuclear Instruments and Methods* **85**, 285 (1970).

[GU78]   S. R. Gunn, A calorimetric determination of the specific power of plutonium-239, *International Journal of Applied Radiation and Isotopes* **29**, 497-499 (1978).

[HY99]   P. Hyman, V. Gupta, and D. Sullivan, Nuclear Materials Safeguards Matrix-Specific Qualification & Continuous Bias Correction Programs, Minutes of the Measurement Evaluation Program Meeting, New Brunswick Laboratory, Argonne, IL, May 26-27, 1999.

[IAEA87]   "In-Field Calibration of Neutron Correlation Counter via Calorimetry and High Count Rate Gamma-Ray Isotopic Abundance Measurements," IAEA-SM-293/126, *Nuclear Safeguards Technology 1986* **2**, 239-249 (1987).

[JA78]   A. H. Jaffey, H. Diamond, W. C. Bentley, D. G. Graczyk, and K. F. Flynn, Half-Life of ^{240}Pu, *Physical Review C*, **18**, 969-974 (1978).

[JO82]   K. C. Jordan, unpublished results, Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio (1982).

[LE00]   J. P. Lestone, T. H. Prettyman, and J. D. Chavez, "Performance of the Skid-Mounted Tomographic Gamma Scanner for Assays of Plutonium Residues at RFETS," Proceedings of the Institute of Nuclear Material Management 41st Annual Meeting, New Orleans, LA, July 16-20, 2000.

[LI87]   C. N. Lindsay, R. E. Sprague, and J. A. Brandenburg, A Measurement Control Study for Tritium Gas, MLM-2441, (1987).

[LO90]   V. L. Longmire, T. L. Cremers, W. A. Sedlacek, S. M. Long, A. M. Scarborough, and J. R. Hurd, "Isotopic Ratios and Effective Power Determined by Gamma-Ray Spectroscopy vs. Mass Spectroscopy for Molten Salt Extraction Residues," *Nuclear Materials Management*, Vol XXXI Proceedings Issue, 1990.

[LU84]   L. L. Lucas, and J. R. Noyce, The Half-Life of Plutonium-240, *International Journal of Applied Radiation and Isotopes* **35**, 173-176 (1984).

[MA78]   A. Macdonald and D. J. Savage, Plutonium Accountancy in Reprocessing Plants by Ceric Oxidation, Ferrous Reduction and Dichromate Titration, *Nuclear Safeguards Technology* 1978, IAEA, Vienna, Austria, 1979, Vol. I, PP. 651-663.

[MA80]   S. F. Marsh et al, "Plutonium-241 Half-Life Determined by Mass Spectrometric Measurements of ^{241}Pu: ^{242}Pu Ratios, *International Journal of Applied Radiation and Isotopes* **31**, 629-631 (1980).

[MA82]   "The Use of Calorimetry for Plutonium Assay," J. A. Mason, UKAEA Report SRDP-R100, 1982

[MA82A]   *Numerical Analysis: A Practical Approach*, Melvin J. Maron, Macmillan Publishing Co., Inc., New York, 1982, pp. 22.

[MA87]   R. L. Mayer, Application of Prediction of Equilibrium to Servo-controlled Calorimetry Measurements, Proceedings of the Institute of Nuclear Materials Management 28th Annual Meeting, Newport Beach, CA, July 12-15, 1987.

[OE67]   F. L. Oetting and S. R. Gunn, A Calorimetric Determination of the Specific Power and Half-Life of ^{241}Am, **29**, 2659-2664 (1967).

[OE68]   F. L. Oetting, "Average Beta Energy of Plutonium-241 by Calorimetry, *Physical Review* **168**, No. 4, 1398-1401 (1968).

[OS76]   D. W. Osborne and H. E. Flotnow, Half-Life of ^{242}Pu from Precise Low Temperature Heat Capacity Measurements, *Physical Review C* **14, No. 3**, 1174-1178 (1976).

[PE88]   R. B. Perry and S. Fiarman, "Recent Developments in Fast Calorimetry," Proceedings of the Institute of Nuclear Materials Management 29th Annual Meeting, Las Vegas, NM, June 26-29, 1988.

[RA01]   C. Aviles-Ramos, "Exact Solution of Heat Conduction in a Two-Domain Composite Cylinder with and Orthotropic Outer Layer," 35th National Heat Transfer Conference, Anaheim, CA, June 10-12, 2001, LA-UR-00-4931

[RE91]   "Passive Non-Destructive Assay of Nuclear Materials," Doug Reilly, Norbert Ensslin, and Hastings Smith, Jr., Eds., NUREG/CR-5550, 1991, pp 641-660.

[RE91A]   "Passive Non-Destructive Assay of Nuclear Materials," Doug Reilly, Norbert Ensslin, and Hastings Smith, Jr., Eds., NUREG/CR-5550, 1991, pp. 620-623.

[RE91B]   "Passive Non-Destructive Assay of Nuclear Materials," Doug Reilly, Norbert Ensslin, and Hastings Smith, Jr., Eds., NUREG/CR-5550, 1991, pp. 221-271.

[RO81]   "Handbook of Nuclear Safeguards Measurements," D. R. Rogers, Eds., NUREG/CR-2078, 1981, pp. 533-550.

[RU77]   C. R. Rudy and K. C. Jordan, "Tritium Half-Life," Mound Facility Report MLM-2458, December 1977.

[RU84]   C. R. Rudy, K. C. Jordan, and R. Tsugawa, Calorimetric Determination of the Half-Life of Plutonium-240, *International Journal of Applied Radiation and Isotopes* **35**, 177-180 (1984).

[RU97]   C. Rudy, D. S. Bracken, P. Staples, L. Carrillo, R. Cech, M. Craft, J. McDaniel, and D. Fultz, "Transportable Calorimeter Measurements of Highly Enriched Uranium," Proceedings of the 38th Annual Meeting of the Institute of Nuclear Materials Management, Phoenix, AZ, July (1997).

[RU98]   C. Rudy, S. Bayliss, D. S. Bracken, J. Bush and P Davis, "Fiber Optic Calorimetry," Los Alamos National Laboratory report LA-13392, (1998).

[RU98A]   C. R. Rudy, S. C. Bayliss, D. S. Bracken, I. J. Bush, and P. G. Davis, "Fiber Optic Calorimetry," Proceedings of the 39th Annual Meeting of the Institute of Nuclear Materials Management, Naples, FL, July (1998).

[RU99]   C. R. Rudy, "Determination of Average U-235 Enrichment and Mass of Uranium Metal without Gamma-Ray Spectroscopy," Proceedings of the 40th Annual Meeting of the Institute of Nuclear Materials Management, Phoenix, AZ, July (1999).

[RU99A]   C. R. Rudy, Correlative Assay of Uranium with Calorimetry, Neutron
            Counting, and Mass Spectrometry Data, *Nuclear Instruments and Methods
            in Physics Research A* **437**, 501 (1999).

[RU00]   C. R. Rudy, J. Briden, M. F. Duff, R. L. Fultz, W. E. Kesling, J. R.
            Wetzel, A. R. Campbell, C. Fellers, and J. F. Lemming, "Automated
            Plutonium Assay System (APAS) Redux," Proceedings of the Institute of
            Nuclear Material Management 41st Annual Meeting, New Orleans, LA,
            July 16-20, 2000.

[RU00A]   C. Rudy, D. Bracken, M. Smith, and M. Schanfein, "Calorimetry of TRU
            Waste Materials," Presentation/Paper at 7th Nondestructive Assay Waste
            Characterization Conference, Salt Lake City, UT, May 23-25, 2000, LA-
            UR-00-1741.

[RU00B]   C. Rudy, D. Bracken, M. Smith, and M. Schanfein, "Calorimetry of TRU
            Waste Materials," Presentation/Paper at Spectrum 2000 International
            Conference, Chattanooga, TN, September 24-28, 2000, LA-UR-00-3761.

[SA64]   A. Savitzky and M. J. E. Golny, *Anal. Chem.* **36**, 1627 (1964).

[SA83]   T. E. Sampson and R. Gunnink, The propagation of errors in the
            measurement of plutonium isotopic composition by gamma-ray
            spectroscopy, *Journal of the Institute of Nuclear Materials Management*,
            XII, no 2., 39-48 (1983).

[SA99]   T. S. Sampson, "Gamma-Ray Isotopic Analysis Development at Los
            Alamos," Los Alamos National Laboratory document, LA-13667-MS,
            November 1999.

[SC00]   Constance M. Schneider, Phillip Hypes, Lu Ann Zook, and Corinne
            Nadalin, "MultiCal Validation and Verification Plan, Version 3.0," Los
            Alamos National Laboratory document LA-UR-99-3603, May 4, 2000.

[SCBI]   Constance M. Schneider and Corinne Nadalin, "MultiCal Software Design
            Document Version 3.0," Los Alamos National Laboratory document LA-
            UR-99-3604 (June 13, 2000),

            Constance M. Schneider, "MultiCal Software Functional Requirements
            Specification Version 3.0," Los Alamos National Laboratory document
            LA-UR-99-3605 (May 5, 2000).

            Constance M. Schneider and Corinne Nadalin, "MultiCal Software
            Implementation Document Version 3.0," Los Alamos National Laboratory
            document LA-UR-99-3606, June 13, 2000.

Rodney S. Biddle, Phillip Hypes, Constance M. Schneider, and Corinne Nadalin, "MultiCal User's Manual Version 3.0," Los Alamos National Laboratory document LA-UR-99-3602, May 10, 2000.

Constance M. Schneider, "MultiCal Software Validation Document Version 3.0," Los Alamos National Laboratory LA-UR-99-4197, June 01, 2000.

Constance M. Schneider and Corinne Nadalin, "MultiCal Software Configuration Management Plan Version 1.011," Los Alamos National Laboratory document, LA-UR-99-4199, January 12, 2000.

[SE78]   P. W. Seabaugh and K. C. Jordan, "Calorimetric Determination of the Half-Life of Plutonium-239," *International Journal of Applied Radiation and Isotopes*, **29**, 489-496 (1978).

[SM00]   M. K. Smith and D. S. Bracken, "The Development of a Multi-Exponential Prediction Algorithm for Calorimetry," Proceedings of the Institute of Nuclear Materials Management 41st Annual Meeting, New Orleans, LA, July 17-20, 2000.

[SM01]   M. K. Smith and D. S. Bracken, Calorimeter Prediction Based on Multiple Exponentials, *Nuclear Instruments and Methods A*, Accepted for publication, 2001.

[SM01A]   Morag K. Smith, Phillip A. Hypes and David S. Bracken, "Thermal Response Based Item Identification," Proceedings of the Institute of Nuclear Materials Management 42nd Annual Meeting, Indian Wells, CA, July 15-19, 2001.

[SP99]   "Calorimetry Exchange Program, Quarterly/Annual Data Report, Calendar Year 1998," prepared by M. Irene Spaletto and David T. Baran, NBL-353, May 1999.

[ST78]   W. W. Strohm, The Measurement of the Half-Life of Plutonium-239 by the U. S. Half-Life Evaluation Committee, *International Journal of Applied Radiation and Isotopes*, **29**, 481-483 (1978).

[ST84]   F. J. Steinkruger, G. M. Matlack, R. T. Beckman, The Half-Life of ^{240}Pu Determined by Specific-Activity Measurements, *International Journal of Applied Radiation and Isotopes*, **35**, 171-172 (1984).

[ST84A]   W. W. Strohm, The Measurement of the Half-Life of Plutonium-240 by the U. S. Half-Life Evaluation Committee, *International Journal of Applied Radiation and Isotopes*, **35**, 155-157 (1984).

[WA77]   A. H. Wapstra and K. Bos, The 1977 Atomic Mass Evaluation, *Atomic Data and Nuclear Data Tables*, **19, No. 3**, (1977).

[WE95]   T. L. Welsh, L. P. McRae, C. H. Delegard, A. M. Liebetrau, W. C. Johnson, W. Theis, R. J. Lemaire, and J. Xiao, "Comparison of NDA and DA Measurement Techniques for Excess Plutonium Powders at the Hanford Site: Statistical Design and Heterogeneity Testing," Proceedings of the 36th Annual Meeting of the Institute of Nuclear Materials Management, New Orleans, LA, July (1995) Vol. XXIV.

[WE95A]   T. L. Welsh, L. P. McRae, C. H. Delegard, W. C. Johnson, W. Theis, R. J. Lemaire, W. Theis, M. S. Krick, J. E. Stewart, and J. Xiao, "Comparison of NDA and DA Measurements Techniques for Excess Pu Powders at the Hanford Site: Operator and IAEA Experience," Proceedings of the 36th Annual Meeting of the Institute of Nuclear Materials Management, New Orleans, LA, July (1995) Vol. XXIV.

[WE97]   J. R. Wetzel, T. E. Sampson, and T. L. Cremers, "Calorimeter in the Aries Recovery System," Proceedings of the Institute of Nuclear Materials Management 38th Annual Meeting, Phoenix, AZ, July 20-24, 1997.